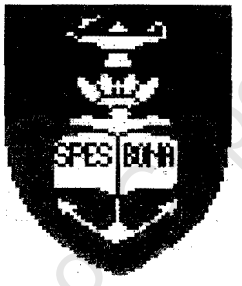
IMPACT ON SOIL CHEMISTRY OF ATMOSPHERIC SULFUR FALLOUT NEAR ARNOT COAL-FIRED POWER STATION, IN THE EASTERN TRANSVAAL HIGHVELD REGION, SOUTH AFRICA

PETER AZAH ABANDA

BSc. (Hons) Geology

University of Buea, Cameroon



Submitted in partial fulfilment of the requirements for the degree of **Master of Science** in

Environmental Geochemistry

University of Cape Town, South Africa.

2000

ACKNOWLEDGEMENTS

I would like to thank my supervisors Dr John Compton and Professor Martin Fey for their invaluable guidance, enthusiasm and encouragement without which this thesis would not have been completed. I also wish to thank Dr. Richard White for his advice on writing and for reading through stuff no matter how crude it was handed to him.

ESKOM, through funding for the research into the sensitivity of the soil environment to the deposition of acidifying air pollutants in South Africa offered financial support.

Aid rendered by the following is also greatly acknowledged:

Mieke van Tienhoven for initiating the research and helping out with sampling in the field, Leslie Petrik for her invaluable support and help with research material, Patrick Sieas for assisting with IC analysis, Benis Egoh for general laboratory assistance, Steve Bainbridge assisted with total carbon analysis, Fran Pocock did all the XRF analysis, Professor William Stock of Botany Department, UCT provided facility for organic carbon analysis, Stewart Whyte provided accommodation during sampling, Sani Chauke for transporting my samples from Arnot to Johannesburg, Lourens Schloemann (environmental manager at Arnot) for help with sampling.

I would also like to thank Masentle Bolofo, Boni Tholoana and Tembisa Mavangwe for all their support.

Many thanks to the guys: Jacob Ndah (Yacuf), Harry Akoh Asana (Rev), Charles Ndanyeh (Moscow) and Musi Ndah Ndah (Justice) for their encouragement and humour.

To Dad, Mom, Martin, Chris, Benson, Angela and Abah, Danco and all my friends I say thank you for your prayers love and support.

Ross and Meris, you were such a wonderful company. I enjoyed the numerous discussions through the year, the good humour and the free computer lessons.

ABSTRACT

Due to the combination of heavy industry and climatic conditions that are unfavourable for dispersion of atmospheric pollutants, the eastern Transvaal Highveld region (Mpumalanga) is considered to be at risk from potential impacts of atmospheric pollution. Knowledge of the destruction caused to European and North American ecosystems by industrial emissions is a warning to developing nations like South Africa with limited resources to combat this damage.

A total of 19 soil profiles were sampled in July 2000 at various distances in an ENE to SE transect around Arnot power station as well as one site due north and another site due south of the power station. The objective of the study was to evaluate the potential impact of atmospheric sulfur deposition on the soils surrounding Arnot power station. In particular, the study focused on the relationship between sulfur and organic carbon (OC) and on the various pools of sulfur in the soil. A representative selection of collected soil samples was characterized both physically and chemically in the laboratory. In addition to the representative soils sampled in 2000, archived soils sampled in 1996 and 1999 from the same area were included in some of the chemical analyses.

The soils in the study area are highly weathered, poorly buffered, well drained and oxidised. Clay content of the samples ranges between 5 and 20 wt % with a mean value of 11.5 wt %. Kaolinite is the dominant clay-size fraction mineral with minor amounts of iron oxides and mica. The soils are generally acidic with the pH in water ranging between 4.9 and 6.5 and the pH in 1 M KCl ranging between 4.1 and 5.0. The pH decreases with soil depth. There is no change in the pH of soil samples collected from the same sites in 1996, 1999 and 2000.

Samples collected in 2000 have KCl extractable acidity that ranges from 1 to 14 $mmol_c/kg$ compared to 0.2 to 10.6 $mmol_c/kg$ for samples collected in 1996. The average base saturation of the 2000 samples (78 %) is slightly lower than the value reported in 1996 (84 %).

Organic carbon content ranges between 0.4 and 2 wt %. The topsoils are enriched in OC with an exponential decrease in OC content below 10 cm depth in all soil profiles. The colorimetric method for determining carbon content of the soils is preferred over the Walkley Black method because it gives more accurate results. Total carbon analysis indicates that all carbon in the soil is essentially organic. The slight increase observed in OC content over the three

year period (1996-1999) in a few samples, may be related to local temporal and spatial variations rather than to increases as a result of atmospheric deposition of sulfur. In the majority of the soils the carbon content stayed essentially the same. No significant changes have occurred in the S/C relationship for the soils around Arnot power station since 1996.

Few soil properties show a distinct trend with distance from the power station. Soils within 3-6 km of the power station appear to have the lowest pH values and the highest soluble sulfate concentration in saturated paste extracts. Soil profile A2 situated 16.6 km from the power station also recorded pH values similar to those within the 3-6 km distance. It is difficult to establish if these observed changes are a result of increased deposition of atmospheric pollutants from Arnot power station or are a result of spatial variation (inhomogeneity).

The general increase in total sulfur with increasing organic carbon content of the soils reflects the fact that the largest sulfur pool is organic sulfur. The organic S/C ratio is fairly constant at a value of 0.02 and suggests a preferential retention or loss of organic sulfur compounds in these soils. Over 80 % of total sulfur in the topsoil is organic sulfur with up to 50 % of total sulfur occurring as adsorbed sulfur in the lower horizons of an iron and aluminium oxide rich soil. The transfer of organic sulfur to adsorbed sulfur with depth in the soil results from microbial degradation of organic matter and the adsorption of released sulfate onto iron oxide surfaces. Soluble sulfur (sulfate) represents a minor fraction of the total sulfur in all soil horizons (< 2 %). It has been shown that there is no significant shift in the relationship between S and C in the samples collected over a four year period from around Arnot power station contrary to early predictions.

TABLE OF CONTENTS

CHAPTER 2

CHAPTER 3

CHAPTER 4

CHAPTER 5

CHAPTER 6

1 INTRODUCTION AND LITERATURE REVIEW

1.1 Introduction

Tyson *et al.* (1988) describe the eastern Transvaal highveld (ETH) (Mpumalanga) as having levels of air pollution comparable to heavily industrialised Northern Hemisphere countries. Most of the air pollution results from coal-fired power stations along with substantial contributions coming from other sources like coal discard dumps, domestic combustion, motor vehicle and small industries. Wells *et al.* (1996) hold that as of 1990, over 97.4% of all SO_2 emissions come from coal-fired power stations. The total SO_2 emission in South Africa for 1993 was estimated at 2.1 million metric tonnes of which over 94% is from the Industrial Highveld Region (Wells *et al.,* 1996). In addition to the high rate of pollutant emission, the ETH has climate conditions that are adverse for the dispersion of atmospheric pollutants, namely: high atmospheric stability, clear skies and low wind speeds generally associated with a high pressure system prevailing over the region (Tyson *et al.*, 1988). Atmospheric pollution on the South African Highveld is therefore a concern because of the combination of heavy industry and climatic features that prevail in the region. The frequent occurrence of surface inversions (80 - 90% of days in the winter months) permits the accumulation of pollutants near ground level. Although industrial stacks, and those of power stations in particular, are generally able to emit gaseous and particulate pollutants above the boundary layer, looping and fumigation of plumes may occur under convective conditions. Under such circumstances, the concentration of pollutants at ground level may be high, especially within 4 km of the stack (Tyson *et al.,* 1988).

Wet deposition of sulfur in the central industrial Highveld has been estimated at about 5.7 kg ha^{-1} yr^{-1} while dry deposition has been estimated at 13.1 kg ha^{-1} yr^{-1} giving a total of 18.8 kg ha^{-1} yr^{-1} (Zunckel, 1998). These levels of dry deposition are comparable to levels obtained by the U.S. Environmental Protection Agency (EPA) Clean Air Status and Trends Network (CASTNet) using the inferential technique for the USA.

1.2 Motivation

A lot of research on the atmospheric dynamics of sulfur and nitrogen oxides and their impacts on aquatic and terrestrial ecosystems have been carried out in Europe and North America (Galloway, 1995). With the growth of this knowledge, the impacts in other regions of the world have been recognised. Fey and Guy (1993) reported an increase in salt concentration in the Vaal dam catchment, resulting from the inability of the soils in the catchment area to retain sulfate from atmospheric deposition. There is therefore a tendency for the salt load in streams draining these catchments to increase as a result of the leaching of this atmospheric input into the rivers through the soils. A steady increase in the salt content of streams in the Mpumalanga area has been reported by Kempster *et al.* (1996) and they speculate that about 80% of measured sulfate input to the Suikerbosrand catchment, (a tributary of the Vaal River) comes from the atmosphere. This increase in stream water salinity is likely to have an adverse impact upon water use in domestic, mining, electricity generation and other process industries (Heynike, 1981).

A classification of the ETH soils into various sensitivity classes based on variables like parent material from which the soils are formed, organic matter content, exchangeable base saturation, sesquioxide fraction, clay mineral content, sulfate adsorption capacity and the amount and duration of acid input, shows that most of the ETH soils are very sensitive to acid deposition (Tyson *et al.,* 1988). A majority of the soils are inherently acidic and it is speculated that current levels of deposition of atmospheric pollutants may significantly increase the acidity in areas where the soils are not cultivated. In cultivated lands, where there is the common practice of liming the soils, acidification does not pose a major threat to the soils since the added lime plays a major role in neutralizing the acidity from the atmosphere (McFee, 1980).

The following potential impacts are evident in soils as a result of anthropogenic sulfur deposition: soil acidification, increase loss of mineral nutrients needed for plant growth (decrease in base saturation), accelerated weathering of minerals, changes in soil biota, mobilisation of aluminium and other metals in soils, and reduced cation exchange capacity of the soil (McFee, 1980). Acidification of soils, lakes and surface streams draining soils impacted by atmospheric sulfur accumulation and decline in forestry production, as witnessed in Europe and North America, are all phenomena related to atmospheric sulfur deposition. Even though a decline in forestry production as a result of sulfur deposition has not been

reported in the ETH region (Tyson *et al.*, 1988), an understanding of the processes involved is important, as this will ensure early detection of impacts and allow the timely implementation of appropriate control strategies or measures. Despite the negative impacts to soils, sulfur deposition to soils is not all bad. Soil sulfur can be beneficial to plants in sulfur deficient soils; sulfur being an important macronutrient for plant growth.

Van Tienhoven (1997) investigated soils adjacent to Arnot coal-fired power station, a sulfur outfall source, with the view of determining a possible acidification gradient and to see if soil sulfur, or some labile fraction of soil sulfate, decreases with distance from the power station. No trends in sulfur accumulation in the soils along the gradient studied was found, however the soils were found to have a capacity to retain sulfur from atmospheric deposition. Soluble sulfate in saturated paste was found to have a maximum occurring within 4-6 km of the power station. It was also evident from the study that background levels of sulfur in soils around Arnot were higher than in soils from other areas in South Africa, remote from sulfur sources. A follow-up study was carried out three years later by Fey *et al.* (1999) and similar results were obtained. However, in the follow-up study, it was discovered that there was a corresponding increase in soil organic carbon with an increase in soil sulfur. It was estimated that about 30-50 kg per ha per annum of sulfur was transferred onto soils around Arnot. This level is significantly higher compared to the levels reported by Zunckel (1998) for greater central Highveld region. There is a slight shift in the sulfur-carbon relationship between the 1996 study and the follow-up study in 1999 (Figure 1.1). The intercept on the Y-axis is similar for the two plots, but the slope of the 1999 plot is slightly steeper suggesting an increase in sulfur content with a corresponding increase in organic carbon. This may also be explained by the fact that, there is enhanced sulfur accumulation in soils rich in organic matter. The majority of the soils studied have had some increase in the soil organic carbon content within the three-year period (Figure 1.2).

A preliminary study of sulfur to carbon ratios in soils of the Mpumalanga region and the southern Kwazulu Natal region of South Africa by Fey and Netch (1994) was unable to find any significant differences between the two regions. It was hypothesised that since soil sulfur significantly correlates with soil organic carbon, and since soil organic carbon content varies from one locality to the other, soil organic carbon can be used as an index to sulfur accumulation from atmospheric inputs. The rationale is that, for a group of soils close to atmospheric emission sources, the intercept of the sulfur-carbon relationship should be greater

(reflecting a larger accumulation of inorganic S) than that for soils remote from air pollution sources. Van Tienhoven (1997) compared this relationship for soils close to emission sources with some soils from non-industrial areas. The results showed that background levels of sulfur were higher near emission sources.

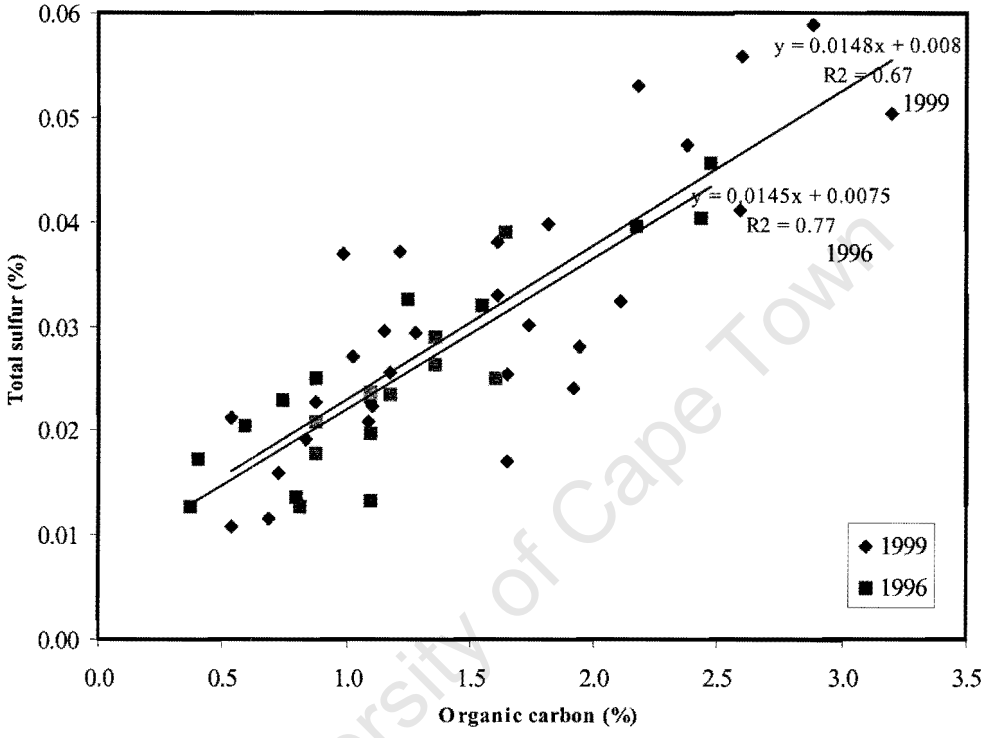


Figure 1.1. Sulfur and organic carbon relationship for soils sampled in 1996 and in 1999 (Fey *et al.*, 1999). (Organic carbon was analysed by the Walkley Black wet oxidation method)

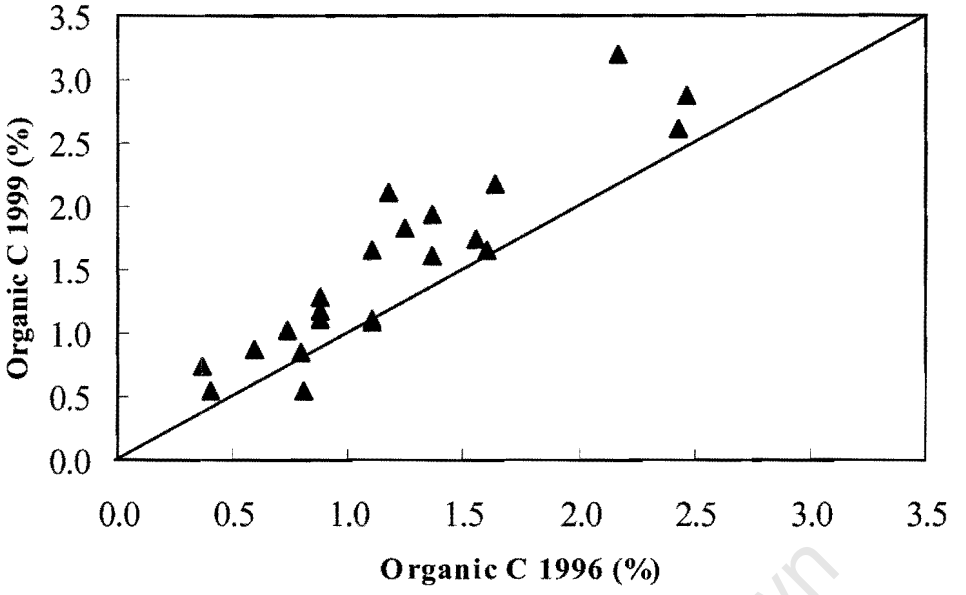


Figure 1.2. Comparison of soil organic carbon for soils collected in 1996 and in 1999 (Fey *et al.*, 1999). (Organic carbon was analyzed by the Walkley Black wet oxidation method).

1.3 Objectives

The current study is aimed at:

- Further investigating the relationship between organic carbon and soil sulfur in soils adjacent to Arnot power station
- Investigating the relationship of pH to other soil variables such as the base saturation, cation exchange capacity (CEC), organic carbon, and extractable acidity.
- Seeing if any spatial differences exist in the sulfur-organic carbon content of the soils and if these are related to position relative to the point source (distance from the power station).
- Investigating vertical gradients in soil profiles of various soil chemical properties and the suspected maximum of soluble sulfate in soil solution extracts within 4-6 km of the power station Van Tienhoven, (1997).

- Improving the database of research on the impacts of air pollution on soils in the ETH region.

1.4 Forms and mobility of sulfur in soils: A literature Review

1.4.1 Sulfur in the atmosphere

Atmospheric sulfur exists in three major forms: hydrogen sulfide (H_2S), sulfur dioxide (SO_2), and sulfate (SO_4^{2-}). Hydrogen sulfide is mainly found over oceans, marshes and swamps, SO_2 comes from fossil fuel burning, oxidation of H_2S and in ore processing, while sulfate is most common as aerosols and constitutes about 20% of atmospheric sulfur (Moss, 1975). Levels of SO_4^{2-} may be higher in maritime locations as a result of sea spays. In the atmosphere, SO_2 and H_2S can be converted to sulfate by either photochemical oxidation in the gas phase or catalytic oxidation in cloud droplets.

1.4.2 Atmospheric sulfur deposition pathways onto soil/vegetation systems

Sulfur enters the soil system from the atmosphere either as sulfate from wet or dry deposition and as SO_2 mainly from dry deposition (Figure 1.3). This fraction of the sulfur transferred to the soil is soluble and is held mainly by soil colloids. Always *et al.* (1937) were the first to show that soils would absorb SO_2 directly from the atmosphere. The soil condition is important in determining the amount of SO_2 that the soil will retain at any particular time. A moist soil with a low pH and high organic matter content will absorb more SO_2 from the atmosphere than a dry soil with alkaline pH (Moss, 1975). Once absorbed, SO_2 will undergo conversion to sulfate similar to the conversion of SO_2 to sulfate in the atmosphere.

Atmospheric SO_2 can also reach the soil through absorption by plant leaves. The type of vegetation cover will determine how much SO_2 can be absorbed from the atmosphere. Zunckel (1998) showed that more SO_2 is transferred to the soil through plant absorption where the vegetation was evergreen and the leaves broad. Once in the plants, SO_2 accumulates as SO_4^{2-} in the spongy mesophyll layer of the leaf cells (Moss, 1975). From the above, it is obvious that sulfate sulfur that can be measured as an indicator of both soil and plant sulfur accumulation, and as a possible key to pollution.

Wet deposition as indicated above is also another means by which sulfate can enter the terrestrial ecosystem. During wet deposition, sulfate is dissolved in rainwater or aerosol

sulfate particles are simply washed down by rain droplets. Wet deposition is a significant source of sulfate input to soils in high rainfall regimes.

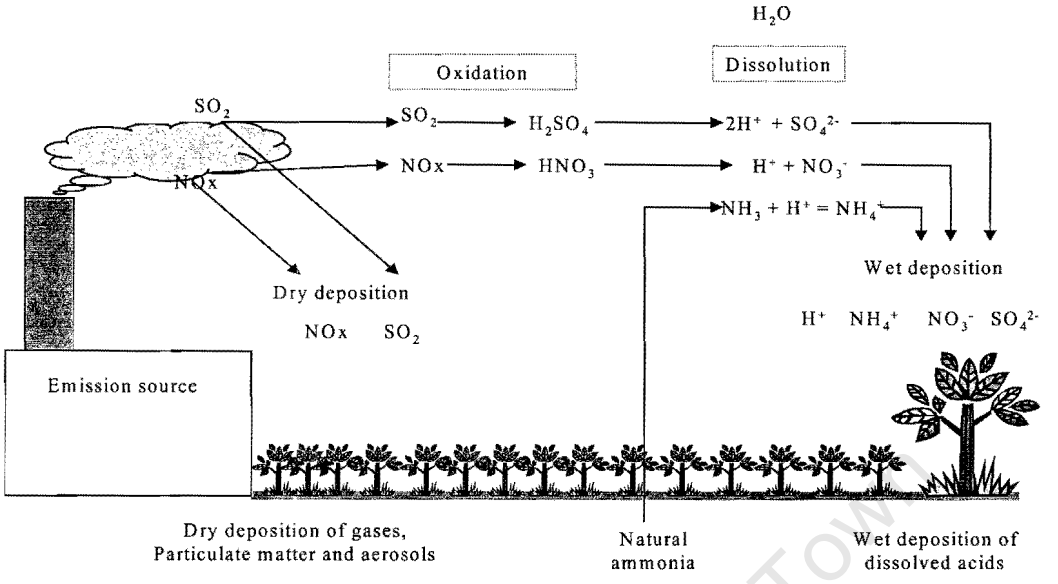


Figure 1.3. Conceptual model of the transfer of air pollutants to soil/vegetation systems (modified from Pidwirny, 1996).

1.4.3 Co-deposition of base cations and particles (alkaline dust) and its potential effect on the deposition of acidity.

The deposition of base cations and alkaline dust and their potential effect on the deposition of acidity is important in studies of soil acidification resulting from deposition of atmospheric pollutant gases (Schaaf *et al.*, 1995 and Larssen and Carmichael, 1999). Base cations and alkaline dust can be derived from various sources: ploughing for agriculture, roads and other building constructions, mining activities and from fly ash. These can contribute in buffering the pH of precipitation as well as topsoil pH in areas affected by acidic deposition.

Over 90% of dust in South Africa comes from the ETH region (Wells *et al.*, 1996). The chemistry of this dust will differ depending on the source. Fly ash from Arnot coal-fired power station is rich in lime and the pH of leachate from this fly ash is >12 (fresh fly ash) (O'Brien, 2000). Acidity resulting from sulphuric acid can be neutralised by CaO according to the following reaction: $CaO + H_2SO_4 \rightarrow Ca^{2+} + H_2O + SO_4^{2-}$.

The neutralisation of acidity by most carbonate materials is quite well documented in the literature. In Northern China, the presence of alkaline dust with a high neutralizing capacity

has resulted in a high precipitation pH despite high sulfur emissions in the area (Larssen and Carmichael, 1999).

ESKOM Technology environmental report of 1999 estimated that about 1496 kg particulate matter was emitted per Gigawatt-hour of energy in 1992. This amount was about half of what was emitted four years before. Total energy production from coal-fired power stations was estimated at 180 Gigawatt-hour in 1999. Exposed ash dams can also contribute substantially to the total particulate matter budget that ends up in the soils around these power stations.

1.4.4 Factors affecting the deposition, retention and mobility of sulfur in soils

Turner *et al.* (1996) presented a review of the processes of atmospheric deposition and the chemistry of this deposition in South Africa. The sulfate anion was shown to be the dominant anion in wet deposition in the ETH region and showed a negative correlation with distance away from the emission source (Figure 1.4).

Wet deposition can easily be measured through rainfall but dry deposition is very difficult and expensive to measure. Dry deposition is usually quantified by the equation:

$Q = \pm V_d.C$, where C is the concentration of pollutant species in the atmosphere and V_d is the deposition velocity. The ± implies that deposition can be from a surface (emission) or to a surface (deposition).

Due to the cost involved in measuring V_d, in South Africa, the inferential model is used in calculation of V_d (Zunckel, 1998). It has been shown that because of the low seasonal rainfall in the area, dry deposition of pollutants remains a very important form of transfer of materials to the surface (Zunckel, 1998).

As acid precipitation percolates into the soil, there is interaction with exchangeable cations on clay, oxide minerals and organic matter in the soil (Drever, 1997). According to the charge balance principle, cations in soils cannot be leached out of the soil system unless an equivalent amount of anions is present in the soil solution. Therefore, the retention of anions in soils will diminish the leaching of base cations as well as of Al^{3+} and H^+ (Seip, 1980). The base saturation can be defined as the fraction of exchange sites occupied by base cations such as Ca^{2+}, Mg^{2+}, Na^+ and K^+. The aluminium ion (Al^{3+}) and H^+ occupy the balance of the exchange sites. Soils therefore with a low sulfate retention capacity will leach out most of the base cations and under extreme cases, aluminium begins to leach out.

Sulfate sorption in soils is negatively correlated with the organic matter content of the soil (van Tienhoven, 1997; Courchesne *et al.*, 1998). The competition between sulfate anion and organic anion for Al binding sites may account for this negative correlation. Courchesne *et al.* (1998) proposed that the impacts of organic matter on sulfate retention are three fold: a direct control through the organic anion competition with sulfate anion and indirect effects through organic matter control on both the vertical distribution and nature of pedogenic iron, aluminium and silicon solid phases. Soils rich in organic matter in the top horizons will therefore have a higher sulfate retention capacity in the lower horizons because of the competition for positively charged sites in the upper horizon between negatively charged organic anions and the sulfate anion.

The rate of impact of sulfur on soils will depend on the rate of deposition, site water balance, pedogenic processes and inherent soil sensitivity. The rate of deposition will depend on the turbulence of the atmosphere, the local meteorological conditions and the impacted surface (Zunckel, 1998). The site water balance will depend on the amount of rainfall in the area and the degree of leaching. Inherent soil sensitivity will depend on such factors like the buffer capacity of the soils (carbonate rich or carbonate poor), the rate of mineral weathering, the exchangeable base status (base saturation), the sulfate absorption capacity and the cation exchange capacity (CEC) of the soils (McFee, 1980). A soil with a high CEC is strongly buffered against changes in pH or leachate composition.

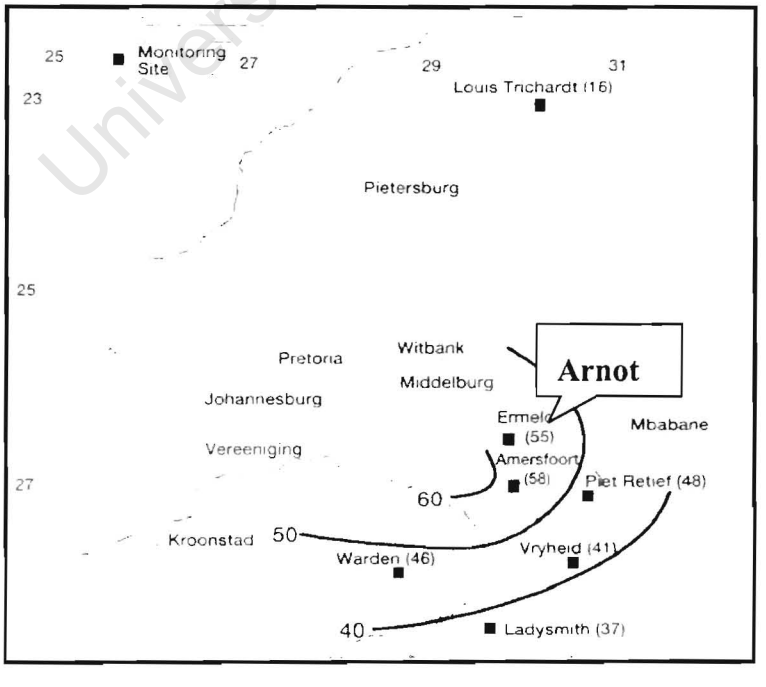


Figure 1.4. Seven year mean sulfate concentration in wet deposition μeq/l (adapted from Turner *et al.*, 1996)

1.4.5 Processes and factors affecting sulfate mobility

1.4.5.1 Anion exchange

Anion exchange, which simply involves the interchange of an anion in solution and another anion on a charged surface, is important in the mobility of sulfate. Most sulfate accumulates in the subsoil where oxides, as discrete particles or as coatings on clays minerals impart positive charge or anion exchange capacity to the soil. At low pH, aluminium and iron oxide surfaces are positively charged (pH dependent charge), and exhibit anion exchange (Drever, 1997). There is preferential adsorption of SO_4^{2-} (divalent anion) to Cl^- and NO_3^- (monovalent anions) but PO_4^{3-} is more strongly adsorbed than SO_4^{2-}. The concentration of phosphate in soil solutions is typically low so the competition for exchange sites with sulfate ions is low.

1.4.5.2 Sulfate reduction

Sulfate reduction is also important in the mobility of sulfate in soils. Sulfate reduction reduces soil acidity but the reverse process, oxidation of sulfides, enriches soil sulfate and increases acidity. Sulfate reduction is locally important but not on a regional scale.

1.4.5.3 Biological mechanism

Biological mechanisms may also play a role in sulfate mobility. The uptake of sulfate by plants results in depletion of soil sulfate and consequent loss of soil acidity. Plant uptake of sulfur will result in the loss of acidity since this will necessitate the excretion of an anion such as OH^- capable of neutralising soil acidity. In industrialised areas, the net uptake of sulfate by plants is far less than the input so uptake is relatively unimportant (Drever, 1997). The uptake of NO_3^- will behave in the same way. However, since the amount of SO_4^{2-} input or NO_3^- far exceeds plant requirements, there is a tendency for accumulation of these anions in the soil (Reuss, 1975).

1.4.5.4 Aluminium sulfate precipitation

Precipitation of aluminium sulfates, jurbanite, $AlOHSO_4$ and alunite, $KAl_3(SO_4)_2(OH)_6$ locks up SO_4^{2-} and prevents it from leaching. Positively charged aluminium and iron oxides at low pH retain more SO_4^{2-} than soils poor in these fractions. Alunite and jurbanite, are more stable than gibbsite in acidic SO_4^{2-} containing waters (Drever, 1997). These minerals can form in soils subject to acid deposition, even though they have not been observed directly their presence has been inferred from soil solution composition (Fey *et al.* 1999b). The present consensus is that alunite and jurbanite are not important in soils affected by acid deposition but they are important in acid mine drainage.

1.4.5.5 Biomass change

Biomass is loosely used to include living plants and non-living organic matter in soils. Plants will take up sulfate from the soil during growth and this sulfate is either returned through leaf fall or when the plants die and decay (mineralization). The production of organic acids (humic and fulvic acids) from decomposition of organic matter will increase the soil acidity. The partial pressure of carbon dioxide in the soil will also increase due to biological activity.

1.4.5.6 Transport of base cations

Acid rain can be neutralised by forest canopy before it reaches the ground. When plants take up base cations they excrete another cation to balance charge in the soil (Drever, 1997). For each proton neutralised in the canopy, a proton is produced in the soil zone and the overall acidity of the system is unchanged (Drever, 1997). Plants therefore serve as a good cycling mechanism for cations in soils by extracting base cations from the deeper soil layers and replenishing the soil with the cation through leaf fall. This situation can be reversed where logging takes place leading to export of base cations from the soil.

1.4.5.7 Chemical weathering

Atmospheric acid deposition can be neutralised over long periods through chemical weathering of rock minerals. Easily weathered rocks such as limestone will replenish the base cations and reduce acidification.

1.4.6 Forms of sulfur in soils

Soil sulfur exists in a variety of forms (mainly organic and inorganic) and oxidation states, and is involved in a variety of chemical and biological reactions, and interacts with the lithosphere, hydrosphere and atmosphere either naturally or as a result of man's interference (Freney and Williams, 1983). In well-drained, well-aerated soils, most of the sulfur is almost entirely in the form of sulfates. Sulfate-sulfur commonly increases with depth in a soil profile. The occurrence of gypsum ($CaSO_4.2H_2O$) in subsoil horizon of many soils is a recognised pedological feature. Sulfides and other sulfur compounds of lower oxidation state than SO_4^{2-} including elemental sulfur can be formed under anaerobic conditions such as occur in tidal swamps and waterlogged soils (Starkey, 1966).

1.4.6.1 Organic sulfur

Sulfur is an essential component of soil organic matter in which it is closely associated with carbon and nitrogen. Normal C:N:S ratios of soils show a global similarity of approximately 10:1:0.1. Differences occur in these ratios, and have been attributed to differences in the parent material, soil forming factors e.g. climate vegetation, leaching intensity, drainage, and temperature or differences in cultivation and management practices (Freney and Williams, 1983). Table 1.1 shows variations in the C:N:S ratios in different soil types from Canada and in Scottish soils derived from diverse parent materials.

Organic sulfur exists mainly as amino acid forms and includes cystine, methionine, cysteic acid, and methionine sulphoxide. Apart from amino acid sulfur, present knowledge only permits a grouping of compounds on a very broad basis, which is believed to relate to the chemical bonding of the sulfur in them. This grouping is based on the reactivity of the soil organic sulfur with certain reducing agents. These are as follows; organic sulfur, which is reduced to H_2S by hydroiodic acid: this sulfur is not bonded to carbon and is believed to be mainly ester sulfur. Organic sulfur, which is not reduced by hydroiodic acid: this sulfur is believed to be bonded directly to carbon (Freney and Williams, 1983). Organic sulfur generally decreases with depth in a soil profile except in soils with organic matter accumulations in the B horizon, for example in the B-horizon of podzols (spodosols) where there is an accumulation or organic acids. In general, hydroiodic acid reducible sulfur accounts for 30-70% of organic sulfur (Freney and Williams, 1983)

Table 1.1. Variation in C:N:S ratios for different soil types and for soils derived from different parent materials (adapted from Freney and Williams, 1983)

Region	Soil type	C:N:S
CANADA	Brown Chernozerm	93: 10: 1.64
	Dark brown Chernozerm	94: 10: 1.54
	Black Chernozerm	113: 10: 1.41
	Grey black transitional	125: 10: 1.32
	Grey wooded	119: 10: 1.56
	Brown Chernozerm	120: 10: 1.41
	Gleysol	156: 10: 2.00
SCOTLAND	**Parent material**	
	Granite	169: 10: 1.45
	Slate	148: 10: 1.42
	Old Red Sandstone	130: 10: 1.37
	Basic Igneous	140: 10: 1.37
	Calcareous	113: 10: 1.27
	Mean	140: 10: 1.38

1.4.6.2 Sulfates

Sulfate exists in soils as water-soluble salts (mainly Na, Ca and Mg salts) and as sulfate ions adsorbed on soil colloids or insoluble compounds. The amount of soluble sulfur varies within soil profiles and between soil types depending on the leaching intensity, drainage and input of soluble sulfate into rainwater, irrigation waters and fertilisers. Generally, the surface of well-drained soils contains only a small amount of soluble sulfate, though under arid and poorly drained soils high levels may accumulate at the surface. Sposito and Reginato (1992) considered the leaching of sulfate, which is the dominant form of sulfur in soil water as a major player in the cycling of nutrient metals such as Ca, Mg, and K, as well as toxic metals, such as aluminium and some heavy metals. Seasonal, fluctuations of soil soluble sulfate may occur in soils with crops or pasture.

The capacity of soils to adsorb sulfate varies greatly. Adsorbed sulfate normally increases with depth in a soil profile (Freney and Williams, 1983). Adsorption is fully reversible and is concentration dependent. Adsorbed sulfate can be irreversibly bound to soils after sampling and air-drying (Karltun, 1994) and this will give lower estimates of this form of sulfur during

analysis. Sulfate adsorption depends on the amount and nature of clay minerals (Ensminger, 1954) and is greatest in soils containing large amounts of aluminium and iron oxides. The amount of adsorbed sulfate present is determined largely by the sulfate adsorption capacity of the soils (Williams, 1974). Adsorbed sulfate may be readily available to plants and in many soils, provides the major source of supply of plant available sulfur. According to Huete and McColl (1984) the net retention of sulfate in soils can result in the reduction of cation leaching.

1.4.6.3 Sulfides

In rocks, most of the sulfur occurs as sulfides e.g. ZnS (sphalerite), FeS_2 (pyrite), PbS (galena), CuS (cuprite), $CuFeS_2$ (chalcopyrite) and the chalcophiles. The sulfides have a very important environmental significance. Sulfides are rare in well-drained and aerated soils but form, an important component of waterlogged or anaerobic soils.

1.4.7 Cycling of sulfur in soils

Sulfur cycling can either be rapid or slow. In sedimentary rocks and coal deposits sulfur has been stored over millions of years. This sulfur only enters the cycle during weathering of sedimentary rocks and during mining and combustion of fossil fuel, mainly coals. Sulfur in the oceans is also cycled in the form of sulfur aerosols or sea sprays and may get onto soil through dry deposition or with precipitation (rainfall or mist and fog). Volcanoes during eruption may also emit an enormous amount of sulfur into the atmosphere as SO_2 gas, which gets to the pedosphere through dry deposition or through rainfall.

Fossil fuel combustion, mentioned earlier, is the major route through which sulfur that was buried in the earth interior over millions of years is today being released into the atmosphere and finally gets into the soil. Over 100×10^6 tons of SO_2 is released to the atmosphere per year with over 93.5% from the Northern Hemisphere countries (Moss, 1975). Some reports show that globally about three times as much SO_2 is emitted into the atmosphere by human action ($\approx$75 Tg S/yr) as by natural processes. It is speculated that future trends of SO_2 emissions will increase substantially in the developing world (Galloway, 1995). Sulfur, which is deposited on the soil from the atmosphere, is removed by crops or can be lost by leaching or erosion, but little is returned to the atmosphere directly. There is, for example, no evidence of a flux of SO_2 from soils or plants to the atmosphere except through burning. Volatile

organic sulfur compounds, including dimethyl sulphide, methyl mercaptan and carbonyl sulphide account for the loss of some sulfur from soils.

1.4.8 Transformation of sulfur in soils

Since sulfur can exist in various states of oxidation, e.g. sulfate (+6), thiosulfate (+6) and -2, elemental sulfur, 0 disulfide and sulfide, -2 (Starkey, 1966), a great variety of transformations are possible. The transformations are usually represented as a cycle. However in reality it is an interwoven network of interrelated reactions. It is generally believed that microorganisms carry out most of the transformations of sulfur although strictly chemical reactions are possible. Microbial transformation of sulfur in soils can be grouped into four main categories:

1. Immobilisation or assimilation of sulfur into organic compounds by plants or microorganisms.

2. Mineralization: i.e. decomposition of organic sulfur compounds.

3. Oxidation of sulfur and inorganic sulfur compounds.

4. Reduction of sulfate and incompletely oxidised inorganic sulfur compounds.

These transformations are affected by the presence of oxygen. The processes of immobilisation, mineralization, oxidation and reduction are concerned with the recycling of sulfur from one pool to another. In the process of immobilisation, microorganisms absorb inorganic sulfur (sulfate) and convert it to organic form for the synthesis of microbial tissue.

Mineralised organic sulfur is used for building new plant tissue and only that part which is not used is released as mineral sulfur. In the presence of abundant organic matter (carbon), available for energy, the entire inorganic sulfur will be converted to some organic form. However if little organic carbon is available, inorganic sulfur will be released from the organic matter.

Freney *et al.* (1970) found that when inorganic sulfur is added to soil, it is converted to organic form within 24 weeks. The cycling of sulfur therefore is a rapid process and takes place within less than a year. Incubation experiments by Fey and Netch (1994) to investigate the incorporation of inorganic sulfur into organic matter by addition of SO_4 to soils treated

with glucose as a carbon source, showed that within 24-36 days most of the inorganic sulfur added is incorporated into organic matter.

By considering the carbon to sulfur ratio in the added material, attempts have been made to determine whether inorganic sulfate will be immobilised or released. Stotzky and Norman (1961) concluded from studies using glucose as a source of carbon that a C:S ratio of 900 or lower would provide adequate sulfur for maximum microbial activity. Therefore, sulfur should not be the limiting factor for the decomposition of organic matter under natural conditions, because most plant residues have C:S ratios less than 900.

1.5 Summary

Sulfur in soils can lead to severe soil acidification, increased loss of soil mineral nutrient (base cations), weathering of minerals, mobilisation of aluminium and other minerals in soils and reduced cation exchange capacity of the soil. The deposition of base cations and particles (alkaline dust) is important in acidification studies because of their role in buffering pH of precipitation and topsoil pH.

Organic sulfur is the major form of sulfur in most temperate soils. The processes of immobilisation and mineralization are important in the transformation of sulfur from one form to the other. A strong negative correlation exists between sulfate sorption and organic matter content of soils due to competition between organic and sulfate anions for positively charged sites on soil surfaces.

It has not yet been established whether an accumulation of sulfur will lead to an increase in the organic carbon content of soils. However the sulfur-organic carbon relationship can be a very useful index for accumulation of sulfur based on the almost uniform C:S ratio for most soils.

2 BACKGROUND TO STUDY AREA

2.1 Locality

Sampling was concentrated, around Arnot coal-fired power station. A number of factors motivated the selection of Arnot power station for the study:

- The station is one of the most easterly of all the power stations in the ETH region and is one of the seven base load power station that is fueled with coal from the Mpumalanga province.
- This power station is the most distant from the Gauteng, Witbank, and Middelburg industrial complexes, and background pollution levels are therefore expected to be lower than at any other power station.
- The station is also one of the oldest in the ETH with its first unit coming into operation in 1971.

2.2 Site selection

The sites sampled for this study had been carefully selected by the initiators of the study into the impacts of air pollution on soils around the Arnot power station (van Tienhoven, 1997). Sites were selected based on meteorological data of the area. The sites were all chosen down-wind in the prevailing winter wind direction to the east of Arnot power station. Other criteria used in the selection of sampling sites were based on accessibility of the sites. Most of them are located close to pans where water and sediment samples were also taken during earlier studies. Some of the sites selected are located on private property and permission was needed for access. The sites were also selected such that they could be revisited for follow-up studies. The selection also minimized as much as possible differences that may come about as a result of the geology, vegetation cover or land use. All the sites were selected in areas with the same land use, i.e. uncultivated land that is not limed and which has stayed undisturbed for extended periods of time. Some of the sites have not been cultivated for over 40 years and the land is only used for grazing of cattle. Detail description of these sites is in the MSc. thesis by van Tienhoven (1997).

Four additional sites were sampled for the current study and these also took into consideration the land use, geology and vegetation cover. The additional sites were aimed at clarifying certain issues raised in the previous studies. For example, two of the sites A16 (3 km) and A17 (4 km) were located downwind in the prevailing wind direction like the previous 15 sites (in an arc ranging ENE to SE of the power station). The remaining two sites, A18 and A19 were located 6 km to the north and 6 km south of the power station, respectively.

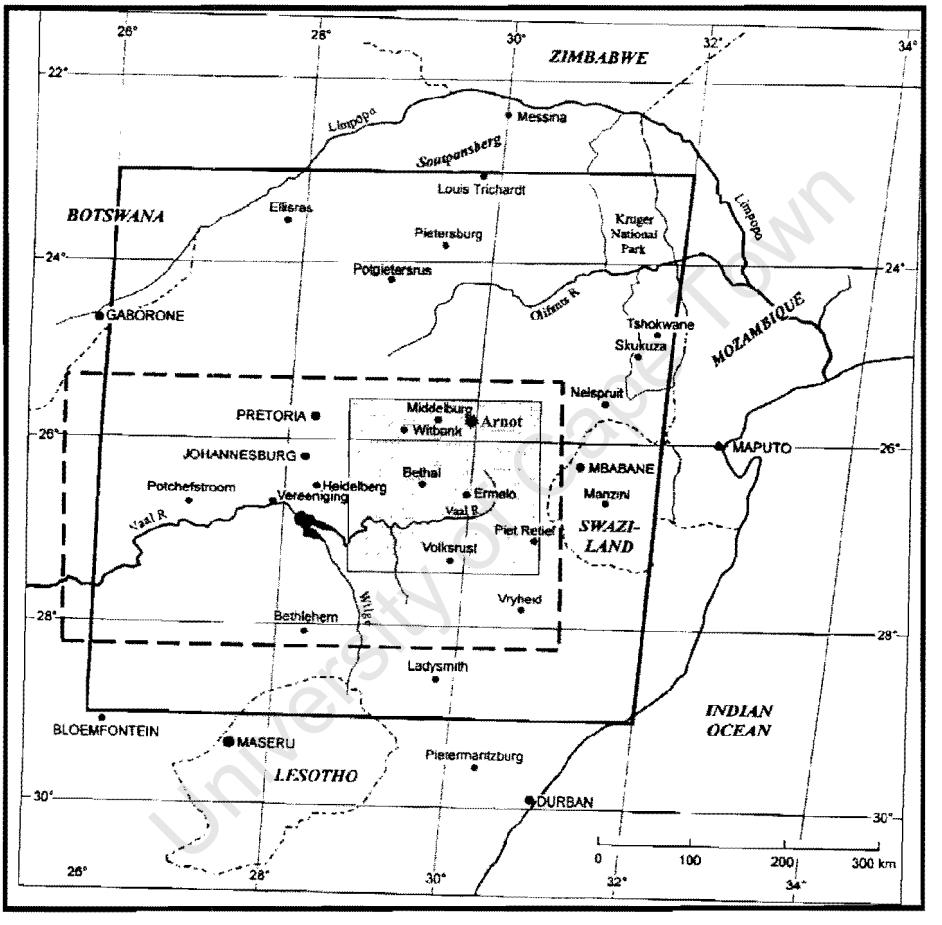


Figure 2.1. Map of study area showing Arnot (star) in relation to greater ETH region (shaded area-solid line).

Figure 2.2. Sampling site located close to a pan looking the power station from a distance.

2.3 Meteorological factors

Atmospheric pollutant dispersion or accumulation will depend to a large extent on the local meteorological factors. Held *et al.* (1996) describe the climate of the ETH region as the most unfavorable for pollutant dispersion in the world. The dominant daytime wind direction in the Mpumalanga area is north to north westerly. Easterly winds are the next most frequent, increasing during winter. At Arnot, the most frequent daytime winds are from the NW 15% of the time followed by westerly winds 12% of the time (Table 2.1). It is expected that the plume will most likely hit the ground in the SE and ESE directions. Sampling was located in an arc ranging ENE to SE of the power station since the winds blow in this direction with a 37% frequency. The climate of the area is subtropical, characterized by very hot summers with afternoon thundershowers and cold dry winters with strong thermal stratification near ground level. The average annual rainfall is about 600-700 mm. Ten years average rainfall data for Bankfontein (geographical coordinates 25° 40'S and 29° 37' E) near Arnot are presented in Table 2.2. The potential evaporation in the area exceeds rainfall. Intense rainfall episodes are common and may cause intensive leaching of material or pollutants from the surface to lower

levels in the soil profile. Such intense episodes of rainfall were registered in 2000 during the months of February and March.

Table 2.1 Percentage frequency of occurrence and mean wind speed for each of the 16 wind directions at Arnot. Data from 1 April 1979 to 31 March 1984 (adapted from Pretorius et al., 1986).

	24-hour Period		Day-time Period 06h00-18h00		Night-time period18h00-06h00	
Wind direction	Frequency of occurrence %	Mean wind speed km/h	Frequency of occurrence %	Mean wind speed km/h	Frequency of occurrence %	Mean wind speed km/h
N	8.7	12.7	3.7	14.3	13.7	12.2
NNE	5.7	11.1	3.0	12.2	8.3	10.7
NE	7.4	13.6	3.8	14.1	11.0	13.4
ENE	11.6	16.4	8.5	17.9	14.7	17.5
E	13.2	18.3	11.6	19.4	14.7	17.5
ESE	5.9	15.3	5.9	16.1	5.9	14.6
SE	2.9	12.3	3.6	13.0	2.2	11.0
SSE	1.7	9.5	2.0	9.9	1.3	8.8
S	2.2	8.9	2.9	9.0	1.4	8.7
SSW	2.6	9.9	3.8	10.3	1.5	8.7
SW	3.9	11.3	5.5	11.7	2.2	10.3
WSW	3.9	12.1	5.6	13.1	2.3	9.8
W	3.3	12.9	4.7	14.7	1.8	8.4
WNW	7.2	15.8	11.9	17.2	2.6	9.2
NW	10.3	15.9	15.2	18.0	5.4	10.1
NNW	9.6	13.8	8.2	6.5	11.0	11.8

Table 2.2 Monthly rainfall data for Bankfontein (data from the South African weather Bureau, Pretoria).

YEAR	*JAN*	*FEB*	*MAR*	*APR*	*MAY*	*JUN*	*JUL*	*AUG*	*SEP*	*OCT*	*NOV*	*DEC*	*ANNUAL*
1990	45.4	119.9	83.9	72.9	8.5	0.0	6.0	3.0	0.0	83.8	111.8	150.0	685.2
1991	250.0	53.7	166.7	0.0	6.2	28.8	0.0	0.0	0.0	62.3	51.6	114.5	733.8
1992	116.0	129.9	32.4	88.2	0.0	0.0	0.0	32.3	28.3	60.1	24.8	200.1	712.1
1993	137.0	130.6	78.0	15.1	13.3	0.1	0.0	0.0	22.6	238.9	148.0	124.8	908.4
1994	100.5	126.0	135.4	12.0	0.0	0.0	0.0	1.8	21.4	54.4	82.1	101.2	634.8
1995	99.4	17.8	128.3	76.1	10.8	0.0	0.0	0.0	16.4	61.3	92.2	194.5	696.8
1996	118.0	229.4	97.1	28.2	20.7	0.0	40.6	13.0	0.0	133.9	56.8	99.7	837.4
1997	175.2	28.4	71.3	38.5	61.6	1.2	4.4	5.9	49.2	120.9	164.3	85.3	806.2
1998	40.9	77.6	53.1	0.0	0.0	0.0	0.0	0.0	70.3	121.7	119.3	146.0	628.9
1999	92.1	56.3	36.9	56.3	30.6	3.7	0.0	7.8	35.7	54.9	124.1	218.4	716.8
2000	na	210.6	190.2	67.4	29.5	21.8	0.0	0.0	12.5	na	na	na	532.0

2.4 Vegetation

The vegetation cover is mostly natural grassland. Sampling sites were restricted to this natural grassland with minimal disturbance from grazing or any agricultural practice (Figure 2.3). Some sites are subjected to bush fires in winter but regrowth is rapid in summer. Vegetation in Figure 2.2 shows no signs of disturbance either from grazing by cattle or exposure to bush fires.

2.5 Soils

Soils are formed from the weathering or breakdown of rocks. The geology therefore is important in determining the nature of soils. A majority of the sampling sites fall on similar geology but for a few exceptions. The soils in the area are mainly sandy loams or loamy sands with a few sandy clay soils all having variable clay contents. The soils are well developed, inherently acidic and also highly leached. The predominance of kaolinite in the clay fraction (van Tienhoven, 1997) lends support to the intense degree of weathering in this area.

2.6 Geology.

The geology of the area consists of interbedded shales, shaly sandstone, sandstone, grit and conglomerates with interbedded tillite and shale of the Ecca Formation and interbedded tillites and shale of the Dwyka Formation. Coarse-grained dolerite intrusions are observed in some areas (Department of Mines, 1978; 2528 Pretoria 1: 250 000 Geological map series, Government Printer, Pretoria). This is the major coal-producing region in the country.

Figure 2.3. Natural vegetation on site A10 in winter (photo taken in July 2000).

2.7 Description of soil profiles

A description of the various soil profiles has been attempted following the South African system of classification (Soil Classification Working Group, 1991). The classification is based mainly on observations made in the field during sampling. Details of the soil profile description are given in the appendix section. Figure 2.4 is a representation of the common soil horizons observed in all the soil profiles sampled for this study. The South African system of classification essentially groups soils into soil forms and families. The grouping into soil forms is based on unique vertical features or sequences of diagnostic horizons and materials. A further division into soil families is based on specific properties like soil color,

soil moisture content, presence or absence of carbonates in the profile. The system has adopted local names, which are sometimes names of the area where the soil type predominantly occurs or preferred name by the Soil Classification Working Group.

A majority of the soils according to this system of classification belong to the Avalon (having an Orthic A horizon overlying a yellow brown apedal B horizon). In a few profiles the B-horizon is underlain by a soft plinthic or hard plinthic horizon and this belongs to the Glencoe Form. Site A 10 belongs to the Milkwood Form having a melanic A (dark or somewhat black) horizon overlying a lithocutanic B horizon. This soil is developed on a dolerite basement and is a young soil compared to the other soils in this region. It is a dark colored soil and the clay mineralogy is dominated by smectite with some iron oxides (van Tienhoven, 1997) as opposed to predominantly kaolinite in the other profiles. Site 1 A has been classified as belonging to the Bainsvlei form having a reddish brown apedal B horizon overlying a soft plinthic horizon.

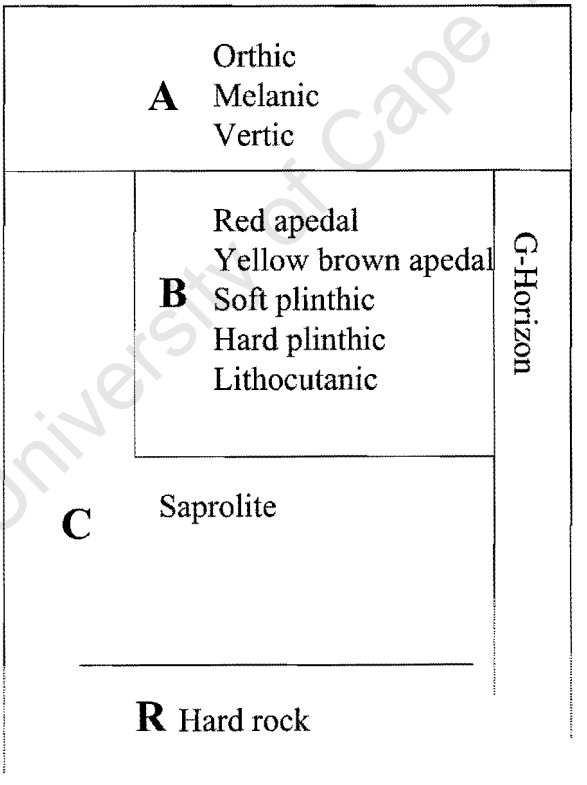


Figure 2.4. Diagrammatic representation of soil profile for sample sites in the study area (modified from Soil Classification working group, 1991)

3 MATERIALS AND METHODS

The following analytical methods discussed below were employed for this study. Bulk air-dried (< 2 mm) soil samples were used in a number of analyses while soil solution extracts were used in others. Each method outlines the sample preparation procedure employed and in some cases reference is made to the appendix for details.

3.1 Materials

3.1.1 Sample collection and preparation

The sampling protocol for this study is different from that of the previous study carried out in 1996. It was aimed at collecting five soil samples from each soil profile at intervals of 10 cm from the surface. At each sampling site, a pit of about 50 cm by 30 cm was dug down to a depth of 50 cm depending on the depth of the particular profile. In some profiles samples were only collected down to a depth of 30 cm. On one site A6, the soil profile was very shallow and only 2 samples could be collected. Samples were scraped with a penknife onto a spade then into a labelled plastic bag and sealed. Figure 3.1 is an example of one of the profiles dug during the sampling exercise. Figure 3.2 also shows the sampling sites in relation to the power station. Analyses were done on the bulk sample, air-dried and sieved (< 2 mm) and on the soil solution. Soil samples collected in 2000 were also used for some analysis as well as archived samples collected in 1996 and 1999 from the same area. The archived samples were all air-dried and sieved (< 2 mm) and stored in plastic sample storage bottles with lids.

3.2 Methods

3.2.1 Soil pH

Soil pH was measured in distilled water, 1M KCl and in saturated paste extracts. Measurements of soil pH in a neutral salt solution are necessary because this compensates for dilution effect. pH was measured with a conventional glass electrode in an equilibrium solution of distilled water and air-dried soil (< 2mm) at a soil: solution ratio of 1:2.5 after ten minutes of equilibration. The same procedure was applied for measuring pH in 1 M KCl solution. pH of saturated paste extracts (prepared by using about 200 g of air dried soil and equilibrating for 24 hrs) was measured immediately after extraction

Figure 3.1 Soil profile of the study area showing an orthic A horizon underlying a yellow apedal B horizon. Some plinthic material is also evident in the figure.

3.2.2 Extractable acidity

KCl extractable acidity was determined according to the method of Thomas (1982). Details are reported in the Appendix A3. A blank of 25 ml 1 M KCl solution was titrated with standard 0.01 M NaOH solution and used as a correction factor. The standard 0.01 M NaOH solution was then used to titrate the supernatant of a 2.5 g air-dried soil sample and 25 ml 1 M KCl mixture. Phenolphthalein was used to indicate the endpoint of pH 8.3. The volume of NaOH needed to neutralise the acidity (corrected for by the result obtained using the blank) was recorded and the number of moles of NaOH was calculated.

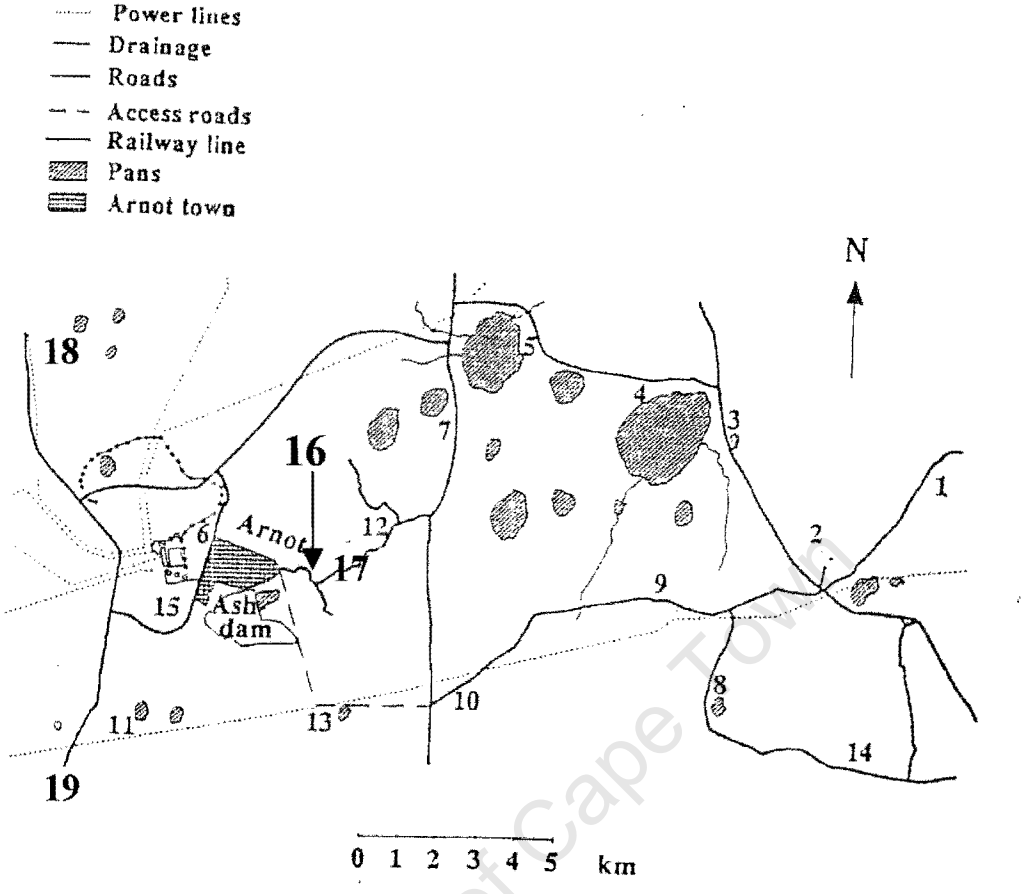


Figure 3.2 Sample collection points. The samples points marked 1-19 are referred to in text as A1-A19

3.2.3 Extractable base cation

Details of the method are reported in the Appendix A4. 10 ml of the centrifuged supernatant solution prepared by equilibrating 2.5 g soil and 25 ml 1M KCl was diluted 10 times. Calcium and Magnesium concentrations were determined in all samples submitted by Atomic Absorption Spectroscopy (AAS) in the Department of Chemical Engineering at the University of Cape Town.

3.2.4 Particle size analysis and mineralogical analysis of the clay size fraction

Exactly 20 g of air-dried < 2 mm soil was used in the particle size analysis. Separation into the different size fractions involved sieving and washing soils through various mesh size sieves. Details of this method are reported in Appendix A9. The separated clay fraction was smeared evenly across a glass slide while still wet and allowed to dry prior to analysis by

XRD. The glass slides were scanned over a 2-theta angle range of 4 – 75°, using a step size of 0.5° and step duration of one second. The samples were irradiated by means of monochromatic X-rays emitted by a copper tube [λ (K_α) = 1.54056 Å]. The generator was run at 25 mA and 40 kV. Reflected x-rays produced characteristic peaks with well-defined d-spaces corresponding to particular minerals.

3.2.5 Major element analysis

Major elements were analysed using powder briquettes prepared according to the standard method applied by the Department of Geological Science at UCT (Appendix A11). The briquettes were analysed on a Phillips PWI 480 wavelength dispersive XRF spectrometer with a dual target Mo/Sc X-ray tube. Iron, Mn and Ti are measured with a tube potential of 100 kV and 25 mA current. The other elements are determined with the tube at 40 kV and 65 mA. Peak only measurements are made on the elements Fe through Mg with backgrounds measured at –2.00 and +2.00°2θ from the peak position. Analytical conditions are given in (Appendix Table A3)

Intensity data are collected using the Phillips X40 software. Matrix corrections are made on the elements Fe through Mg using the de Jongh model in the X40 software. Theoretical Alpha coefficients used in the de Jongh model for all other elements on the analyte element are calculated using the Phillips on-line ALPHAS programme. Na_2O is not included in the matrix correction in the de Jongh model, and no matrix corrections are made to sodium intensities (when fusion discs are used).

3.2.6 Major soluble ions

Saturated pastes were prepared according to the method described by Rhoades (1982). Major cations and anions in the saturated paste extracts were analysed using a Dionex, DX300 series ion chromatograph after filtering the samples through a 0.45μm millipore cellulose acetate micro filter membrane. The following major ions were determined: cations (Na^+, K^+, Ca^{2+}, Mg^{2+} and NH_4^+) and anions (Cl^-, F^-, SO_4^{-2}, NO_3^-, PO_4^{-3} and SO_4^{2-}). Samples were diluted such that their electrical conductivities were around 100 mS/cm.

3.2.7 Determination of organic carbon and total carbon

Many techniques have been used to analyse soil organic matter but the methods reviewed by Nelson and Sommers (1982), i.e. dry and wet combustions for total soil carbon and wet oxidation for soil organic carbon, have been widely adopted. The dichromate wet oxidation

technique first introduced by Walkley (1935) has been modified from time to time depending on the soil type. Many workers have employed correction factors (ranging from 1-2) in the determination of soil organic carbon (Fey *et al.*, 1999a; Nowicki, 1997). Most workers have adopted an average correction factor of 1.3. This average factor of 1.3 was reported to recover about 77% organic carbon average from a selection of 20 British and foreign soils (Walkley and Black, 1934). The recovery of organic carbon has been found to vary between soils and within soils profiles and this has motivated experimental determination of a recovery factor for individual soils or soil profiles.

The soil samples collected around Arnot coal-fired power station in 2000 have been analyzed along with archived soils originally collected from the same area in 1996 and 1999. The archived samples were stored in plastic containers with lids in a soil storage room at the University of Cape Town. Various methods were employed to determine soil organic carbon. The hot digestion/colorimetric wet oxidation method involving controlled heating of the samples and acclaimed for giving better estimates of organic carbon in soils was employed. The dry oxidation method that converts all the carbon in a sample into CO_2 was also employed and used as a standard to check the efficiency of the hot digestion/colorimetric method.

3.2.8 Organic carbon

Organic carbon was determined for three sets of soils collected in different years from the same area. These included archived soil samples obtained in 1996 and 1999 and soils collected in 2000. A subset of soils from the same soil collection was analysed for total carbon at the Soil Science Institute Laboratories in the Department of Agriculture, Cedara, Pietermaritzburg. Organic carbon analyses were done for three full soil profiles (A1, A12 and A18) for the 2000 samples and the rest had topsoil and subsoil analysed. Topsoil (0 - 10 cm) and subsoil (20 - 40 cm) samples obtained in 1996 and 1999 were also analysed where available.

Organic carbon analyses were done by the wet oxidation technique of Baker (1976) in which a mixture of potassium dichromate and concentrated sulfuric acid are used. The method follows the following reaction:

$$2\ Cr_2O_7^{2-} + 3\ C^{o} + 16\ H^{+} = 4\ Cr^{3+} + 3\ CO_2 + 8\ H_2O$$

The addition of excess dichromate allows the amount of organic carbon in soils to be determined either by measuring the excess unreacted dichromate or the concentration of

chromic ions (Cr^{3+}) produced. Excess dichromate can be determined by titration while Cr^{3+} can be determined colorimetrically. The colorimetric method used for this study, involves heating the mixture of soil and acidified dichromate solution at 150°C for 30 minutes. Heat was applied to ensure complete oxidation of all organic carbon in the sample. Further details of this method are in Appendix A6.

3.2.9 Total carbon

Total carbon was determined by the Dumas method for the determination of total carbon, nitrogen and sulfur in soils (Bremner and Mulvaney, 1982). This involves roasting the sample at a temperature about 850°C that converts all the carbon in the sample to CO_2 that is then measured by infrared detection. Further details of the method are given in Appendix A7. Seven samples were chosen from each batch of samples and these were used to serve as standards in evaluating the efficiency of the wet oxidation method. The samples selected were those in which a significant difference in the organic carbon concentration had been observed in the 1999 study.

3.2.10 Soluble sulfate from saturated paste extracts

Exactly 200 g of air-dried soil sample was used to prepare saturated paste according to the standard method of Rhoades (1982). After adding enough water just to completely saturate the soil, the mixture was allowed to equilibrate overnight before extraction. Vacuum extractions was employed, the extracts were filtered through a 0.45 μm millipore cellulose acetate filter membrane and then diluted if necessary before submission for major ions analysis by ion chromatography.

A Dionex 300-ion chromatography was used for the determination of sulfate in the saturated paste extracts. Peak areas were used as for determination of ions concentrations.

3.2.11 Adsorbed sulfate

Van Tienhoven (1997) describes experiments in which ion chromatography was employed to analyse the sulfate in dilute phosphate extracts of soils from around Arnot power station. The study showed that ion chromatography is a more reliable technique than turbidimetry in determining extractable sulfate and gives good reproducible results.

There is, however, a problem to be considered in the extraction of adsorbed sulfate using a phosphate solution. If the soil has a strong tendency to adsorb phosphate, then the capacity of the solution to exchange sulfate will be lessened (M.V Fey, 2000 pers. comm). This constraint

might reduce the capacity of the solution in exchanging sulfate for phosphate on soil surfaces. It is therefore worth experimenting with phosphate solutions of different strengths. A soil with a low phosphate sorption capacity will thus effectively be extracted by a less concentrated phosphate extractant solution, and vice versa. For this reason, the extractant concentration should be kept as high as possible. A 0.01 M $Ca(H_2PO_4)_2$ solution was used for this study suitable for extracting sulfate from most soils (Tabatabai, 1982)

25 ml of phosphate solution was added to 2.5 g of air-dried soil and the mixture put on a reciprocating shaker for 16 hours. The mixture was then centrifuged at 3000 rpm for 5 minutes, filtered and diluted before analysis by ion chromatography.

3.2.12 Total sulfur

Total sulfur was determined by X-ray fluorescence spectroscopy (XRF). Samples were prepared according to the standard methods employed by the Department of Geological Sciences, University of Cape Town. Further details of the method and instrument parameters can be found in Appendix A11.

4 RESULTS

This chapter briefly presents the results of soil chemical analysis. General soil characterisation results are also presented here. In some cases trends as well as relationships between soil chemical properties are highlighted. A discussion of the results follows in the next chapter.

4.1 pH and electrical conductivity (EC)

Results of soil pH in water, 1 M KCl and of saturated paste extracts are presented in Table 4.1. The results show that the soils are acidic with pH in distilled water ranging between 4.9-6.5. The range in the topsoil is between 4.9 and 6.0. The minimum pH value of 4.9 in topsoil was registered in soil profile A16 (3 km form Arnot) and A6 (1.3 km from Arnot) while the maximum topsoil pH of 6.0 was for soil profile A18 6 km north of Arnot Power station. The pH in 1 M KCl ranged between 4.1 and 5.0. In the topsoil, the range is between 4.1 and 4.9. The value of 4.1 is registered in soil profile A16 while that of 4.9 is for soil profile A18. The difference between the pH in distilled water and the pH in 1 M KCl solution (ΔpH KCl) is about 1 pH unit. Figure 4.1 shows the relationship between soil pH in distilled water and in 1 M KCl.

The pH of the saturated paste extracts was slightly higher on the average than the pH measured in distilled water. The range was between 5.0 and 6.4. The maximum pH (6.3) in the topsoil was also registered at soil profile A18 while the minimum pH 5.1 was for soil profile A16. No trends of pH with distance from the power station were observed.

There was a decrease in pH with depth for most of the profiles studied. The change in soil pH with depth for three soil profiles is plotted in Figure 4.2.

The electrical conductivity of the saturated pastes extracts was measured immediately after extraction. The EC ranges between 104 and 432 μS/cm. Broadly similar ECs were obtained for the majority of the soils. The EC is higher in the topsoil and decreases with soil profile depth (Table 4.1).

4.2 KCl extractable acidity

Extractable acidity was determined together with the major extractable base cations, namely calcium and magnesium. Extractable acidity ranged from 1 to about 14 $mmol_c/kg$. There was an increase in acidity with depth in all the profiles studied. Figure 4.3presents data for

selected soil profiles. This increase with depth is matched by a corresponding decreased in soil pH with depth (see section 4.1 above). Acidity in the lower horizons of sites A18 and A19 was much lower than in the other sites.

Table 4.1 Soil pH in distilled water (pH (H_2O), 1M KCl solution, pH (KCl) and pH of saturated paste extracts (pH SPE), electrical conductivity of saturated paste extracts (EC) and KCl extractable acidity (EA) data (2000 soil samples).

Sample	Dist. from power station (km)	EA (mmol/kg)	pH (KCl)	pH (H_2O)	pH SPE	EC SPE (uS/cm)
A1 (0 -10)		2.6	4.6	5.7	5.6	300
A1 (10- 20)		4.4	4.5	5.5	5.6	183
A1 (20- 30)	19.9	6.7	4.4	5.4	5.6	124
A1 (30- 40)		9.8	4.3	5.2	5.7	106
A1 (40- 50)		13.3	nd	5.0	5.6	109
A2 (0-10)	16.9	3.5	4.5	5.2	5.5	346
A2 (30-40)		13.9	4.2	4.8	5.5	204
A4 (0-10)		1.1	4.8	5.7	5.6	262
A4 (10- 20)	12.8	1.6	5.0	6.0	5.6	177
A4 (20-30)		10.1	4.8	5.9	6.0	134
A6 (0-10)	1.3	6.0	4.3	4.9	5.4	186
A6 (10-20)		11.0	4.2	4.9	5.2	nd
A12 (0- 10)		8.6	4.2	5.2	5.3	239
A12 (10- 20)	5.5	13.1	4.1	5.1	5.3	136
A12 (20- 30)		12.9	4.1	5.1	5.7	123
A12 (30- 40)		12.1	4.1	4.9	5.8	104
A16 (0- 10)	3	8.1	4.1	4.9	5.1	381
A16 (20 - 30)		8.2	4.2	5.0	5.3	162
A17 (0-10)		5.1	4.3	5.2	5.4	208
A17 (30 - 40)	4	6.9	4.2	5.0	5.5	120
A18 (0- 10)		1.2	4.9	6.0	6.3	432
A18 (10- 20)		1.0	4.9	6.4	nd	nd
A18 (20- 30)	6	1.0	5.0	6.5	6.4	151
A18 (30 - 40)		1.4	4.7	6.2	6.2	141
A18 (40- 50)		3.7	4.3	5.7	5.8	124
A19 (0- 10)		2.1	4.6	5.3	5.5	259
A19 (10- 20)		0.9	4.9	5.9	6.2	156
A19 (20- 30)	6	3.3	4.3	5.1	5.5	151
A19 (30- 40)		7.7	4.2	4.8	5.1	118

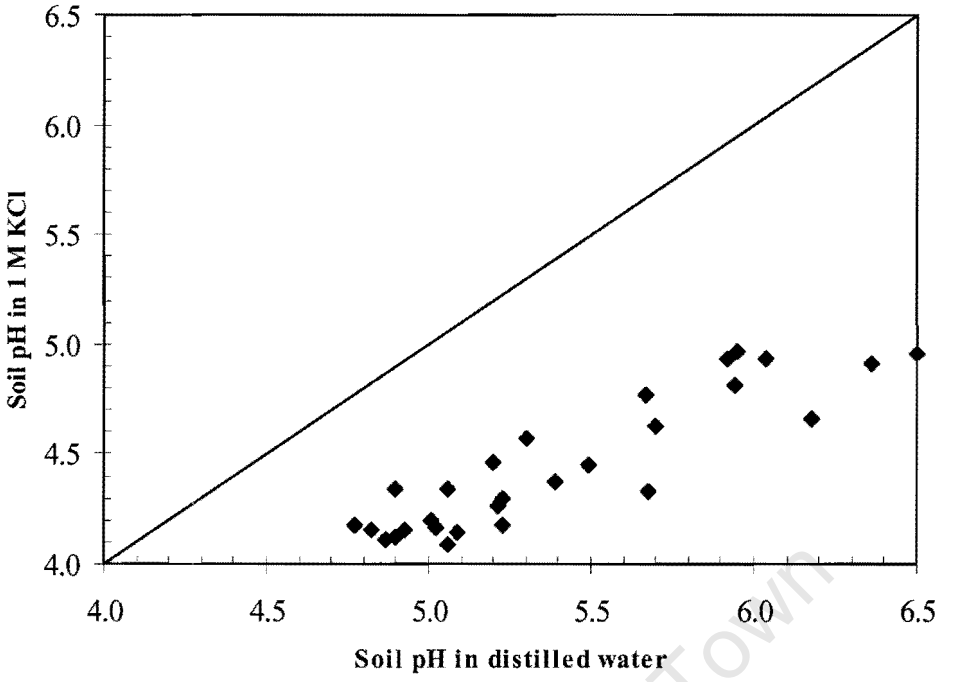


Figure 4.1 The relationship between soil pH measured in distilled water and in 1 M KCl (solid line is an equivalence line).

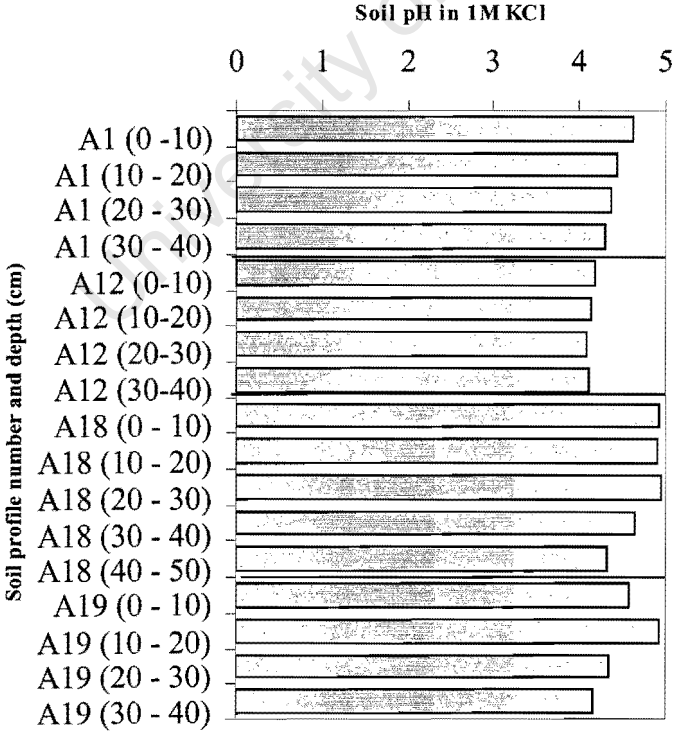


Figure 4.2 Change in soil pH in 1 M KCl with depth for selected soil profiles.

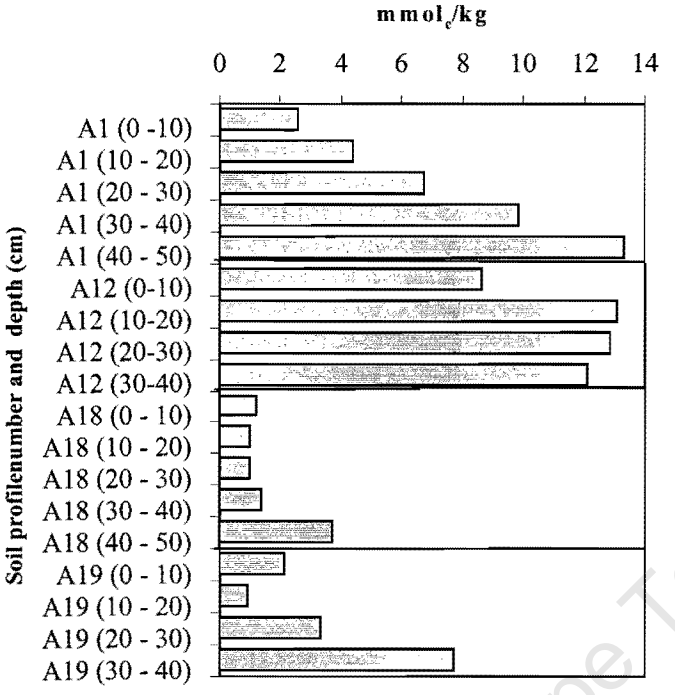


Figure 4.3 Change in extractable acidity with depth for selected soil profiles (mmol$_c$/kg)

4.3 Extractable base cations

Extractable base cation data are presented in Table 4.2. In all the samples analyzed, extractable Ca was higher than extractable Mg. Calcium concentration ranged between 155 and 780 mg/kg of soil while that of Mg ranged between 22 and 335 mg/kg of soil. The concentrations showed no trends with distance from the power station. Extractable Ca and Mg concentration both decreased with soil profile depth. Figure 4.4 represents the change in Ca and Mg with depth for four soil profiles.

Table 4.2 KCl extractable base cations data for soil samples collected in 2000

Sample	(mg/kg)	
	Ca	Mg
A1 (0 -10)	476	169
A1 (10 - 20)	377	139
A1 (20 - 30)	323	122
A1 (30 - 40)	263	81
A1 (40 - 50)	216	56
A2 (0-10)	365	96
A2 (30-40)	208	29
A4 (0-10)	780	335
A4 (10 - 20)	461	327
A4 (20-30)	227	22
A6 (0-10)	343	52
A6 (10-20)	244	30
A7 (0 - 10)	520	122
A7 (30 - 40)	278	80
A12 (0 - 10)	422	94
A12 (10 - 20)	308	57
A12 (20 - 30)	287	60
A12 (30 - 40)	155	57
A16 (0 - 10)	412	75
A16 (20 - 30)	284	44
A17 (0 -10)	334	69
A17 (30 - 40)	254	68
A18 (0 - 10)	640	194
A18 (10 - 20)	536	143
A18 (20 - 30)	500	119
A18 (30 - 40)	362	84
A18 (40 - 50)	294	68
A19 (0 - 10)	345	77
A19 (10 - 20)	417	58
A19 (20 - 30)	326	39
A19 (30 - 40)	219	22

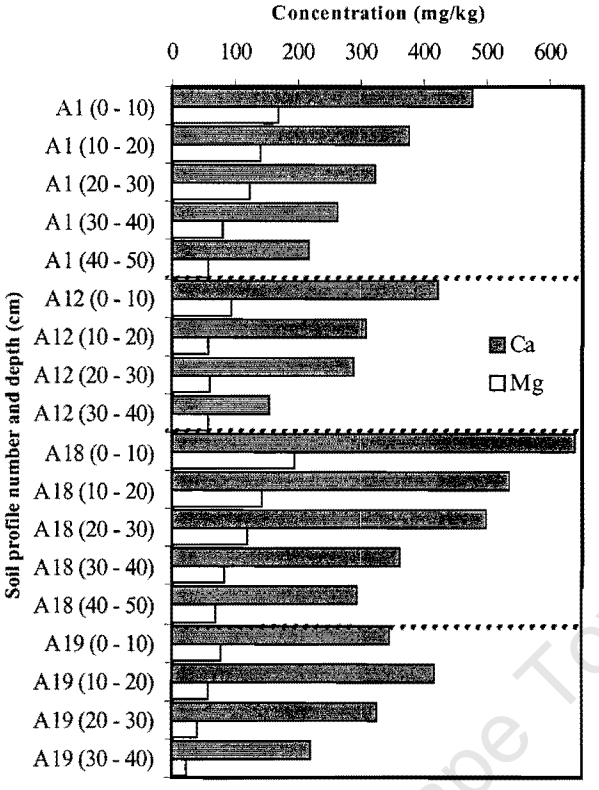


Figure 4.4 Change in concentration of exchangeable Ca and Mg with depth in four soil profiles.

4.4 Particle size analysis and mineralogical analysis of the clay size fraction

A representative collection of soils was used for this analysis. Particle size data are presented in Table 4.3. The sand fraction ranged between 60 and 85%. Mean clay content was about 11.5% (n=8) and ranged between 5 and 20%. The sand content is highest in the topsoil (0-10 cm) of the soil selection studied. The clay content increases with depth. The silt content ranged from 9.5-28%. In all four profiles no clear trends were observed as to how the silt content behaves with soil depth. Clay mineralogical analysis showed a dominance of kaolinite in the clay fraction with minor phases of quartz, mica and iron oxides (goethite, hematite) (Figures 4.5-4.8). The mineralogy remained essentially the same within different soil horizons from the topsoil to the lower soil horizon in all the profiles studied.

Table 4.3 Particle size distribution for selected soil profiles.

Samples	Sand (%)	Silt (%)	Clay (%)
A 1 (0-10)	72.9	17.5	9.6
A 1 (20-30)	60.5	28.0	11.5
A 1 (40-50)	60.4	24.5	15.2
A 12 (0-10)	66.3	26.3	7.5
A 12 (10-20)	71.5	18.3	10.2
A 12 (20-30)	72.4	16.2	11.5
A 18 (0-10)	65.7	nd	nd
A 18 (20-30)	69.8	13.0	17.2
A 18 (40-50)	66.0	13.7	20.4
A 19 (0-10)	85.8	9.4	4.9
A 19 (10-20)	84.3	10.1	5.7

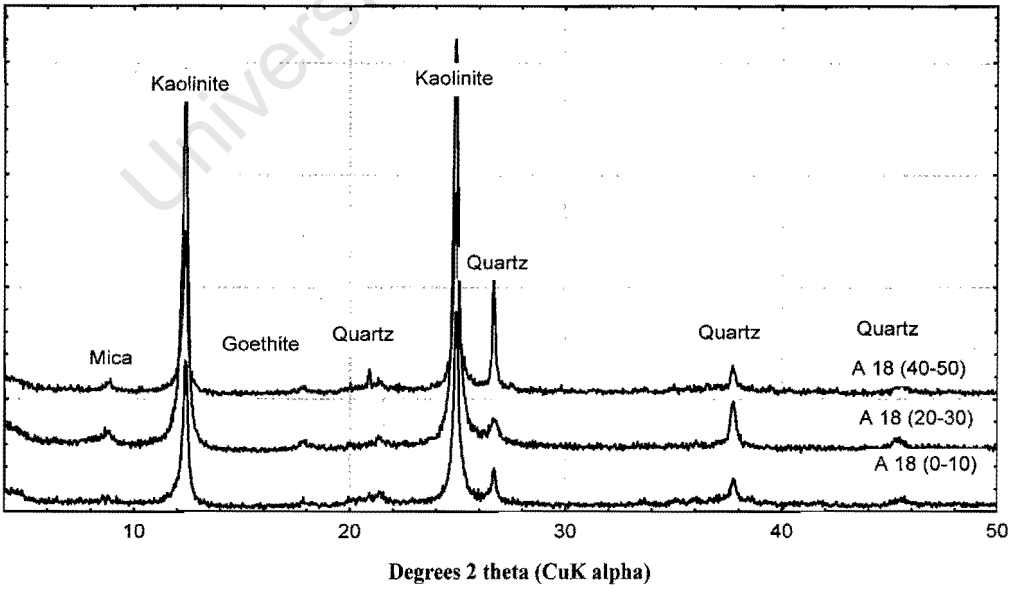


Figure 4.5 XRD scan of the clay size fraction of sample A 18 indicating mineralogy.

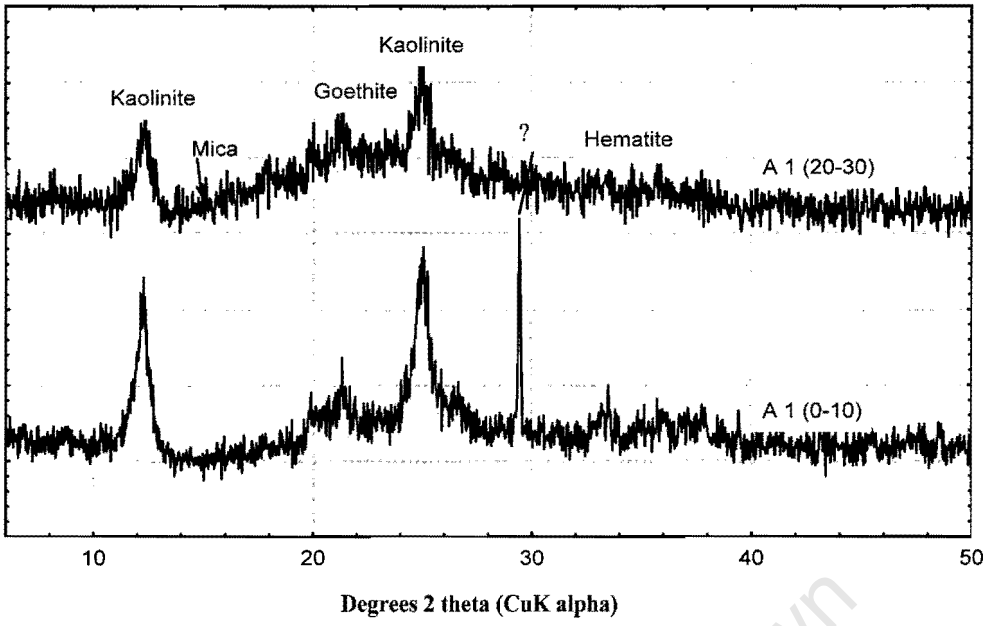


Figure 4.6 XRD scan of the clay size fraction of sample A1 indicating mineralogy.

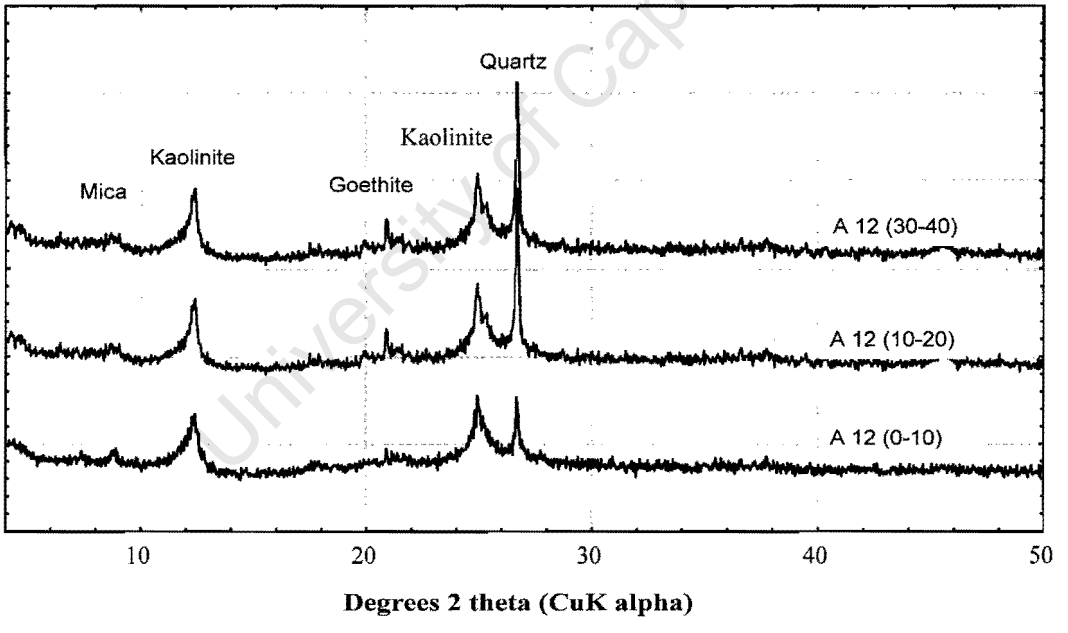


Figure 4.7 XRD scan of the clay size fraction of sample A12 indicating mineralogy.

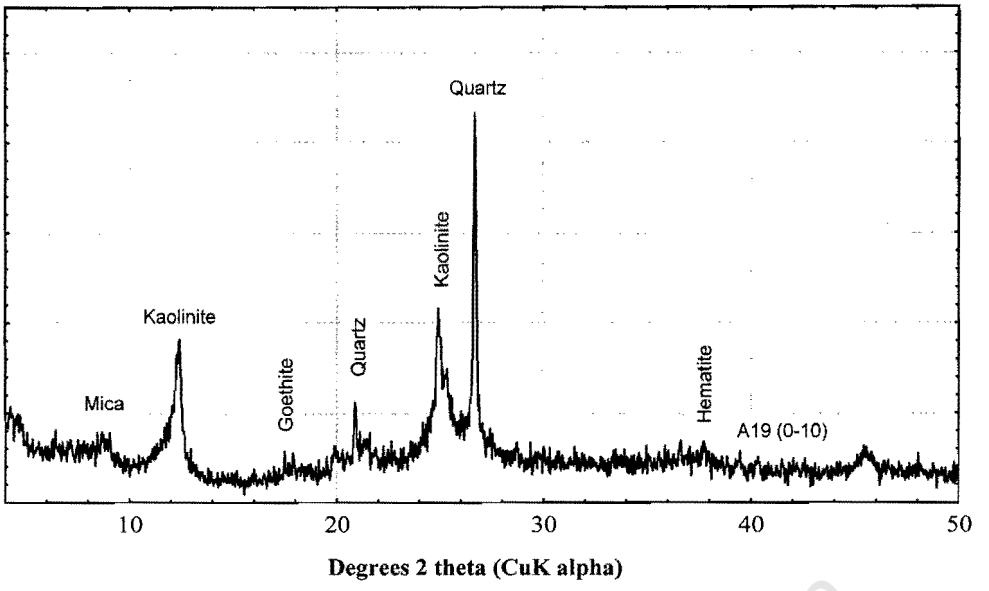


Figure 4.8 XRD scan of the clay size fraction of sample A19 (0-10) indicating mineralogy.

4.5 Major elements

Results of the following major elements (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, and P) are presented in Table 4.4. Silica dominates in all the soils. There was a trend of decreasing amount of SiO_2 with depth. The relative amounts of the oxides are different for each sample. Over 80% of samples A15, A18, A19 are dominated by SiO_2 while sample A1 had approximately 60% SiO_2 but a higher percentage of Al_2O_3 than the rest of the samples. There is a noticeable decrease with depth of the silica fraction from major element analysis, which conforms to trends of decreasing sand fraction with depth from the particle size analysis results. However, iron oxide and aluminium oxide content generally increase with depth.

Soil moisture content and loss on ignition (LOI) were determined for all samples analyzed for major elements by XRF (Table A2 Appendix). Moisture content ranged from 0.3-6% with a mean of 1.2% while the LOI range from about 2-11%. The moisture content appeared higher in the topsoils than in the subsoils while the LOI showed a reverse trend with higher LOI registered in the topsoils and lower LOI in the subsoils.

Table 4.4 Major elements analysis data for soil samples collected in 2000 (%).

Sample	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	TOTAL
A 1 (0 -10)	69	0.9	10.9	7.9	0.12	0.20	0.10	0.03	0.61	0.10	90
A 1 (10 - 20)	66	0.9	12.1	8.0	0.10	0.21	0.06	0.04	0.61	0.08	88
A 1 (20 - 30)	67	0.9	11.8	8.2	0.10	0.19	0.04	0.02	0.58	0.07	89
A 1 (30 - 40)	65	1.0	12.4	8.3	0.09	0.21	0.03	0.04	0.61	0.07	88
A 2 (0-10)	86	0.5	5.5	1.8	0.02	0.10	0.06	0.03	0.40	0.07	95
A 2 (30-40)	83	0.7	7.4	2.1	0.01	0.11	0.01	0.05	0.53	0.04	94
A 3 (0-10)	91	0.6	3.9	1.3	0.03	0.11	0.06	0.15	1.52	0.05	98
A 3 (30-40)	89	0.7	5.0	1.4	0.02	0.16	0.06	0.15	1.63	0.05	98
A 4 (0-10)	65	1.3	12.3	8.4	0.08	0.62	0.15	0.07	1.22	0.10	89
A 4 (20-30)	62	1.3	14.5	9.4	0.06	0.65	0.08	0.04	1.20	0.09	89
A 5 (0-10)	81	0.7	8.5	2.8	0.02	0.14	0.06	0.06	0.89	0.06	94
A 5 (20-30)	73	1.0	12.2	3.3	0.01	0.19	0.03	0.08	1.21	0.05	91
A 6 (0-10)	80	0.8	8.0	3.3	0.02	0.09	0.06	0.04	0.34	0.10	93
A 6 (10-20)	78	0.8	8.8	3.5	0.02	0.09	0.03	0.04	0.34	0.09	91
A 10 (0-10)	73	0.9	7.2	4.7	0.20	0.52	1.21	0.49	0.83	0.07	89
A 10 (30-40)	59	0.9	11.5	7.7	0.20	1.32	2.82	0.76	0.67	0.08	85
A 12 (0 - 10)	79	0.7	7.5	2.6	0.01	0.15	0.08	0.08	0.77	0.07	91
A 12 (10 - 20)	83	0.6	6.8	2.6	0.01	0.24	0.12	0.09	0.66	0.05	94
A 12 (20 - 30)	84	0.6	6.7	2.5	0.01	0.11	0.03	0.04	0.63	0.04	94
A 15 (0 - 10)	83	0.7	7.4	1.9	0.01	0.09	0.07	0.04	0.40	0.09	94
A 15 (20 - 30)	83	0.7	7.6	1.9	0.01	0.07	0.02	0.03	0.36	0.05	94
A 16 (0 - 10)	81	0.9	8.2	2.3	0.02	0.09	0.07	0.05	0.57	0.07	93
A 16 (20 - 30)	82	0.9	8.1	2.1	0.01	0.07	0.03	0.05	0.55	0.06	94
A 17 (0 -10)	84	0.6	5.7	1.1	0.01	0.07	0.04	0.11	1.22	0.04	93
A 17 (30 - 40)	87	0.7	7.3	1.3	0.01	0.09	0.02	0.10	1.27	0.03	98
A 18 (0 - 10)	78	0.7	7.7	2.3	0.02	0.13	0.15	0.04	0.49	0.10	90
A 18 (10 - 20)	80	0.7	7.8	2.3	0.02	0.12	0.11	0.04	0.47	0.07	92
A 18 (20 - 30)	83	0.6	7.0	2.2	0.01	0.10	0.07	0.03	0.40	0.05	93
A 18 (30 - 40)	82	0.7	7.8	2.3	0.01	0.10	0.05	0.04	0.42	0.05	93
A 18 (40 - 50)	81	0.7	8.9	2.5	0.01	0.11	0.04	0.04	0.46	0.05	94
A 19 (30 - 40)	91	0.3	3.2	1.4	0.01	0.08	0.07	0.04	0.18	0.06	97

4.6 Major soluble ions

4.6.1 Major anions

The following anions were analyzed (SO_4^{2-}, Cl^- and NO_3^-). The concentration of soluble anion increased according to the following order: SO_4^{2-} >Cl^-> NO_3^- (Table 4.5). The concentration of SO_4^{2-} and chloride show similar patterns in most soil profiles studied decreasing with depth with maximum concentration occurring in the topsoil (0-10 cm). NO_3^- showed a different trend from that observed for Cl and SO_4^{2-}. The concentration of nitrate was somewhat higher in the subsoils than in the topsoils.

4.6.2 Major cations

The following cations (Ca^{2+}, Mg^{2+}, K^+, Na^+, and NH_4^+) were determined in the saturated paste extracts (SPE). Data for major soluble cations are presented in Table 4.6. In general calcium was the dominant cation in SPE for a majority of the profiles with Mg and K dominating in a few. The topsoils (0-10 cm) are enriched in most of the cations relative to the lower soil horizons. No apparent trend of increasing or decreasing concentration of cations with distance from the power station was observed. Sites A10 and A18 show higher concentrations of Ca than the rest of the profiles.

Table 4.5 Soluble anions concentration in saturated pastes extracts ($mmol_c/l$).

Sample	SO_4^{2-}	NO_3^-	Cl^-	Sample	SO_4^{2-}	NO_3^-	Cl^-
A 1 (0-10)	0.56	0.10	0.99	A 12 (20-30)	0.26	0.33	0.19
A 1 (10-20)	0.44	0.09	0.57	A 12 (30-40)	0.14	0.23	0.24
A 1 (20-30)	0.27	0.12	0.35	A 13 (0-10)	0.54	0.07	0.49
A 1 (30-40)	0.17	0.14	0.33	A 13 (10-20)	0.29	0.09	0.23
A 1 (40-50)	0.07	0.11	0.55	A 13 (20-30)	0.30	0.19	0.31
A 2 (0-10)	0.73	0.47	0.92	A 13 (30-40)	0.30	0.24	0.28
A 2 (30-40)	0.94	0.23	0.20	A 16 (0-10)	2.25	0.16	0.41
A 3 (0-10)	0.48	0.10	0.52	A 16 (10-20)	0.90	0.31	0.16
A 3 (30-40)	0.13	0.17	0.17	A 16 (20-30)	0.59	0.25	0.17
A 4 (0-10)	0.32	0.12	0.54	A 17 (0-10)	0.77	0.09	0.53
A 4 (10-20)	0.32	0.10	0.40	A 17 (10-20)	0.45	0.15	0.19
A 4 (20-30)	0.22	0.16	0.21	A 17 (20-30)	0.24	0.35	0.39
A 5 (0-10)	0.43	0.12	0.87	A 17 (30-40)	0.36	0.16	0.22
A 5 (20-30)	0.42	0.21	0.26	A 18 (0-10)	1.09	0.12	1.20
A 6 (0-10)	0.42	0.12	0.49	A 18 (20-30)	0.26	0.08	0.24
A 10 (0-10)	0.79	0.09	0.53	A 18 (30-40)	0.24	0.29	0.26
A 10 (10-20)	0.46	0.08	0.36	A 18 (40-50)	0.25	0.23	0.25
A 10 (20-30)	0.46	0.07	1.06	A 19 (0-10)	0.57	0.29	1.01
A 10 (40-50)	0.93	0.09	0.53	A 19 (10-20)	0.33	0.26	0.31
A 12 (0-10)	0.64	0.28	0.50	A 19 (20-30)	0.49	0.15	0.23
A 12 (10-20)	0.37	0.35	0.29	A 19 (40-50)	0.31	0.17	0.24

Table 4.6 Soluble cation concentration in saturated paste extracts ($mmol_c/l$)

Sample Name	Ca^{2+}	Mg^{2+}	K^+	Na^+	NH_4^+
A 1 (0-10)	0.76	0.51	0.91	0.27	0.19
A 1 (10-20)	0.55	0.36	0.54	0.26	0.19
A 1 (20-30)	0.49	0.30	0.54	0.25	0.25
A 1 (30-40)	0.22	0.17	0.33	0.16	0.17
A 1 (40-50)	0.56	0.19	0.21	0.27	0.15
A 2 (0-10)	0.70	1.04	1.10	0.22	0.43
A 2 (30-40)	0.19	0.27	0.42	0.57	0.29
A 3 (0-10)	0.68	0.52	0.51	0.08	0.35
A 3 (30-40)	0.27	0.13	0.18	0.10	0.12
A 4 (0-10)	0.82	1.73	0.57	0.11	0.26
A 4 (10-20)	0.74	0.56	0.37	0.23	0.30
A 4 (20-30)	0.23	0.39	0.15	0.13	0.14
A 5 (0-10)	0.49	0.91	0.67	0.11	0.26
A 5 (20-30)	0.26	0.39	0.36	0.14	0.22
A 6 (0-10)	0.60	0.55	0.37	0.07	0.35
A 10 (0-10)	2.75	1.15	0.40	0.46	0.20
A 10 (10-20)	2.05	0.84	0.19	0.45	0.14
A 10 (20-30)	2.07	0.85	0.94	0.43	0.07
A 10 (40-50)	3.13	2.04	0.11	0.67	0.08
A 12 (0-10)	0.46	0.52	0.57	0.21	0.47
A 12 (10-20)	0.29	0.29	0.34	0.21	0.31
A 12 (20-30)	0.20	0.26	0.20	0.18	0.34
A 12 (30-40)	0.14	0.18	0.11	0.22	0.32
A 13 (0-10)	1.10	0.43	0.58	0.18	0.32
A 13 (10-20)	0.73	0.29	0.33	0.18	0.28
A 13 (20-30)	0.81	0.26	0.27	0.32	0.27
A 13 (30-40)	0.71	0.28	0.27	0.29	0.24
A 16 (0-10)	1.50	1.63	0.41	0.21	0.39
A 16 (10-20)	0.62	0.66	0.16	0.13	0.39
A 16 (20-30)	0.48	0.59	0.15	0.11	0.29
A 17 (0-10)	0.63	0.71	0.41	0.18	0.68
A 17 (10-20)	0.43	0.48	0.16	0.15	0.24
A 17 (20-30)	1.01	0.32	0.10	0.34	0.17
A 17 (30-40)	0.45	0.28	0.19	0.23	0.20
A 18 (0-10)	2.17	1.50	1.84	0.54	0.58
A 18 (20-30)	0.58	0.34	0.86	0.19	0.21
A 18 (30-40)	0.41	0.19	0.63	0.08	0.00
A 18 (40-50)	0.34	0.18	0.55	0.18	0.12
A 19 (0-10)	1.44	0.96	0.53	0.46	0.39
A 19 (10-20)	1.25	0.39	0.10	0.37	0.21
A 19 (20-30)	0.54	0.35	0.23	0.22	0.25
A 19 (40-50)	0.24	0.15	0.11	0.13	0.35

4.7 Soil carbon

4.7.1 Organic carbon.

Organic carbon data for soils collected in 2000 are presented in Table 4.9. Results for samples obtained in 1996 and 1999 are presented later in chapter 5 (Tables 5.1 and 5.2). The organic carbon content ranges from about 0.4 to about 2%, with the topsoil (0 - 10 cm) having a higher organic carbon content in all the profiles studied. Mean concentration in the topsoil was 1.1% (n=14) for soil samples collected in 1996 and 1.3% (n=13) in the 1999 soil samples.

Broadly similar results were obtained for the samples collected in 2000. Mean OC content is 1.4% (n=13) for topsoil samples and ranges between 0.6 and 2%. The entire soil collection (i.e. including lower horizon soil samples) OC content ranges between 0.4 and 2.0%.

There was no trend of increasing or decreasing organic carbon content with distance from the Arnot power station. Sample A19 situated 6 km south of the power station, registered the lowest amount of OC (0.6%) in the topsoil compared to the average value of 1.4% of all topsoil samples collected and analyzed. Organic carbon decreased with depth in all the soil profiles studied. The organic carbon content decreases sharply below a depth of 10 cm (Figure 4.9).

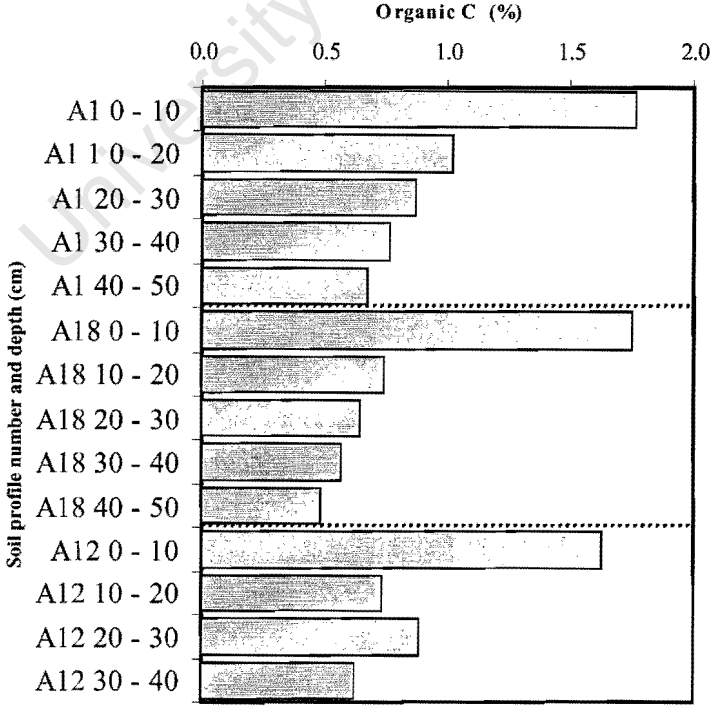


Figure 4.9 Change in organic carbon content with depth for three soil profiles (A1, A12 and A18) in soils obtained in 2000.

4.7.2 Total carbon

Total carbon analyses (dry combustion method) were undertaken to use as standards to evaluate results obtained from organic carbon analyses by the hot digestion/colorimetric method. Total carbon results were similar to those obtained for OC. In a single sample (A7), out of the seven samples selected from each batch of samples, the total carbon percent was lower than the organic carbon. The results of total carbon are presented in Table 4.7. However the observed differences in two of the three samples fall within the uncertainty in the measurements.

Table 4.7 Total carbon (TC) and organic carbon (OC by the hot digestion/colorimetric technique) data for a selection of soils obtained at different times from the same area.

Sample	OC 1996	TC 1996	OC 1999	TC 1999	OC 2000	TC 2000
A 1	1.7	1.8	1.7	1.9	1.5	1.8
A 2	0.4	0.5	nd	0.5	1.3	nd
A 7	1.0	0.9	1.4	1.0	1.0	0.9
A 8	1.0	1.3	1.1	1.3	1.4	1.5
A 10	1.7	1.9	1.9	2.2	1.6	1.9
A 12	1.1	1.9	1.6	1.9	1.2	1.7
A 15	0.9	1.0	1.0	1.0	0.9	0.8

4.8 Soil sulfur

4.8.1 Soluble sulfate

Results for sulfate and other major anions in saturated paste extracts were presented in Table 4.5). The range of sulfate concentration was between 0.32 and 2.35 $mmol_c/l$. The lowest sulfate concentration in the topsoil was recorded at a soil profile situated about 13 km downwind from the Arnot power station while the highest concentration came from a soil profile located about 3 km downwind of the power station (A16). A number of complete soil profiles were analyzed to examine the variation in soluble sulfate concentration with depth. It was observed that most profiles show a similar trend of decreasing water-soluble sulfate with depth. The highest concentration of water-soluble sulfate was recorded in the first 10 cm in the majority of the profiles studied. The concentration decreased sharply below the first 10 cm depth for the majority of the profiles (Figure 4.10).

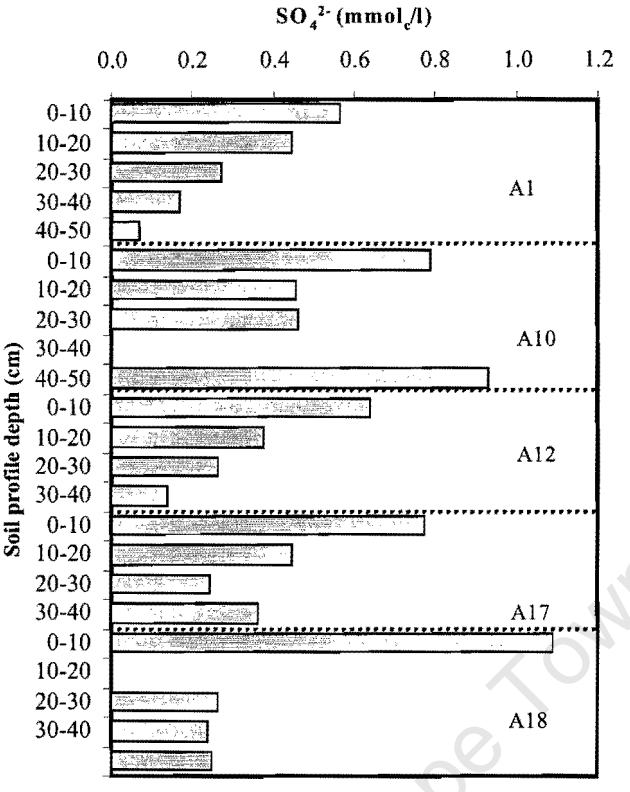


Figure 4.10 Change in soluble sulfate concentration with depth in selected soil profiles.

4.8.2 Adsorbed sulfate

Results for adsorbed sulfate are presented in Table 4.8. Due to time constraints only a limited number of samples were investigated. In this study, because of the relatively low concentration of sulfate in the soils, some problems were encountered with the large extractant phosphate concentration. Large phosphate peaks were recorded in the IC analysis that in a few cases prevented the resolution and quantification of the sulfate peaks. Figure 4.11 (sample A18 0-10) is a chromatogram obtained from analysing dilute phosphate extract by ion chromatography. In the figure, the tailing of the phosphate peak beneath the sulfate peak is evident. There might be a small error associated with this method due to the overlap between the phosphate and the sulphate peaks.

The concentration of extractable sulfate ranges between 121 and 474 mg/kg. Higher concentration of adsorbed sulfate was observed in the lower horizon of profile A1 a red sesquioxide rich soil (Figure 5.9 A1, chapter 5). Profile A19, a sandy soil with very low clay content (~ 5%) also registered a high concentration of extractable sulphate in the lower

horizon (Figure 5.9 A19, chapter 5). Site A18 gave contrasting results to those obtained for Sites A1 and A19. The concentration of extractable sulfate was higher in the top horizon than in the lower horizon (Figure 5.9 A18, chapter 5).

Table 4.8 Concentration of phosphate extractable sulfate in soils analyzed by ion chromatography.

Sample	mg/kg	Duplicates (mg/kg)
A1 (0-10)	180	168
A 1(10-20)	324	345
A1 (20-30)	312	
A1 (30-40)	474	468
A4 (0-10)	130	
A4 (10-20)	127	
A18 (0-10)	191	
A18 (10-20)	bdl	
A18 (20-30)	80	
A18 (30-40)	bdl	
A18 (40-50)	121	
A19 (0-10)	156	
A19 (10-20)	bdl	
A19 (20-30)	nd	
A19 (30-40)	192	
A19 (40-50)	331	

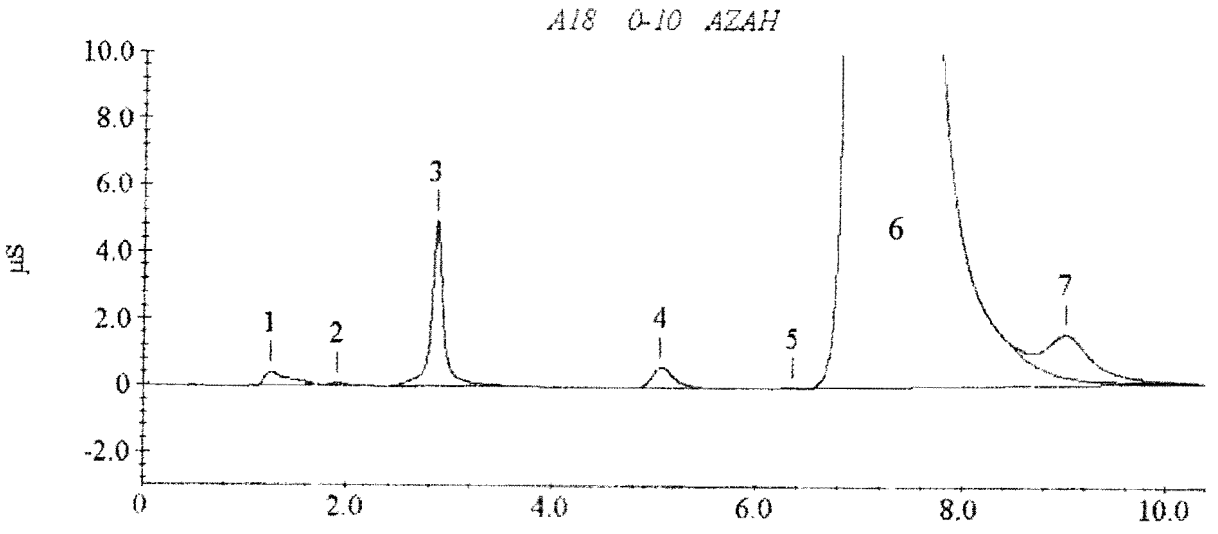


Figure 4.11 Chromatogram for samples A 18 (0-10). Large phosphate peak (6) tailing beneath the sulfate peak (7).

4.8.3 Total sulfur

Total sulfur concentrations are given in Table 4.9. The concentration of sulfur ranged from about 100 to over 400 mg/kg. Concentrations greater than 400 mg/kg in the topsoil were recorded at the following sites A1, A4, A10, A12, A16 and A18. The lowest sulfur content was registered at site A19 located 6 km south of Arnot power station. Generally, higher sulfur contents were registered in the topsoils while lower sulfur contents occurred in the subsoils (Figure 4.12). Higher sulfur contents occurred in soils with higher organic carbon content. Site A19 has the minimum sulfur content and also has the lowest carbon content in the topsoil. No apparent trend of increasing or decreasing sulfur with distance from the power station was observed. Profile A1 situated about 20 km away from the power station recorded the highest concentration of total sulfur in the topsoil (424 mg/kg).

Table 4.9 Total sulfur and organic carbon data for 2000 soil samples (OC analyzed by the hot digestion/colorimetric method)

Sample ID	S (mg/kg)	% OC	S/OC	Sample ID	S (mg/kg)	% OC	S/OC
A 1 (0 -10)	424	1.8	0.02	A 12 (10 - 20)	260	0.7	0.04
A 1 (10 - 20)	338	1.0	0.03	A 12 (20 - 30)	198	0.9	0.02
A 1 (20 - 30)	304	0.9	0.03	A 15 (0 - 10)	219	1.0	0.02
A 1 (30 - 40)	312	0.8	0.04	A 15 (20 - 30)	173	0.6	0.03
A 2 (0 - 10)	253	1.3	0.02	A 16 (0 - 10)	408	1.3	0.03
A 2 (30 - 40)	254	0.4	0.06	A 16 (20 - 30)	212	0.7	0.03
A 3 (0 -10)	135	0.9	0.01	A 17 (0 -10)	228	1.0	0.02
A 3 (30 - 40)	85	0.6	0.01	A 17 (30 - 40)	131	0.5	0.03
A 4 (0 - 10)	411	2.2	0.02	A 18 (0 - 10)	427	1.8	0.02
A 4 (20 - 30)	262	1.1	0.02	A 18 (10 - 20)	256	0.7	0.03
A 5 (0 - 10)	256	1.2	0.02	A 18 (20 - 30)	161	0.6	0.03
A 5 (20 - 30)	241	0.7	0.03	A 18 (30 - 40)	138	0.6	0.02
A 6 (0 - 10)	248	1.0	0.02	A 18 (40 - 50)	152	0.5	0.03
A 10 (0 -1 0)	404	1.9	0.02	A 19 (0 - 10)	133	0.6	0.02
A 10 (30 - 40)	215	1.0	0.02	A 19 (30 - 40)	115	0.7	0.02
A 12 (0 - 10)	415	1.6	0.03				

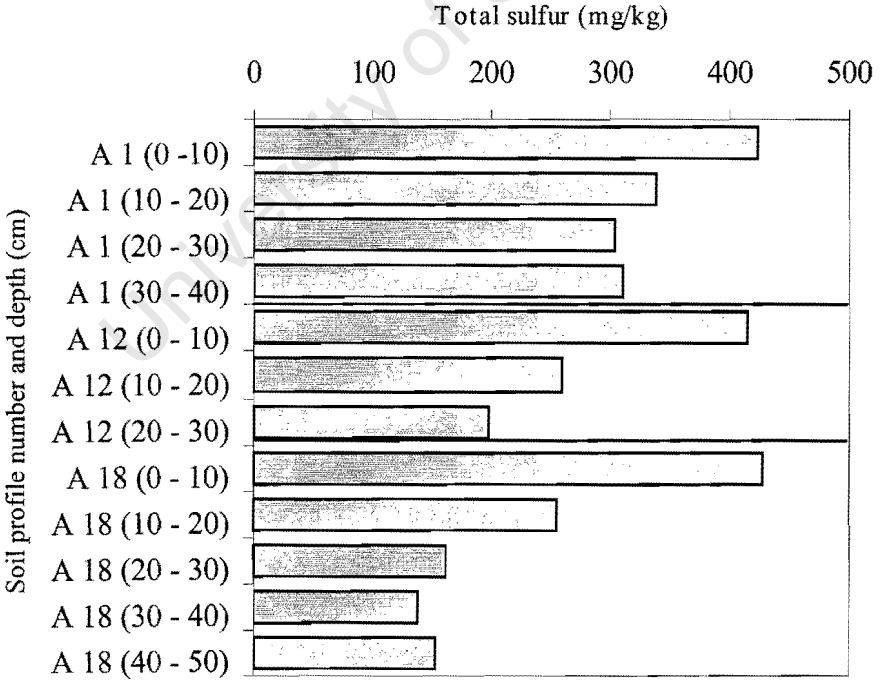


Figure 4.12 Change in total sulfur content with depth for selected soil profiles.

5 DISCUSSION

In this chapter, the results of soil analysis are discussed. Trends in soil chemical properties as well as the relationship between various soil chemical properties are investigated in an attempt to look for any evidence of organic matter accumulation in the soils resulting from atmospheric deposition of sulfur. Attempts have also been made in using relationships such as that between total soil sulfur and organic carbon to see if there has been any significant change in the sulfur and carbon status of these soils within the last four years. Other relationships have also been sought to find out if there is any movement of sulfur into deeper soil horizons and in what form is the bulk of soil sulfur found. Soil properties that can be used as an index to atmospheric sulfur deposition have also been investigated.

5.1 Particle size analysis and mineralogical analysis of the clay fraction

Particle size analysis refers to the measurement of the proportions of the various sizes of primary soil particles as determined by their capacity to pass through sieves of various mesh sizes or by their rates of settling in water (Carter, 1993). The proportions are usually represented by the relative weights of particles within stated size classes.

Particle size analyses (Table 4.3) reveal interesting data in conjunction with the bulk major elemental composition of the samples (Table 4.4). The sand fraction is highest in the topsoil (0-10 cm) of all the profiles studied. The clay fraction on the other hand is highest in the lower soil horizon. Major element analyses show a decrease with depth of the silica fraction (see chapter 4.5). This is in agreement with the results obtained from particle size analysis (sand fraction decreasing with depth). However, the iron oxide and aluminium oxide content show an increase with depth. The implication is that the sand fraction is made up mainly of silica (quartz) while the clay fraction is associated with Al and Fe (probably in the form of aluminosilicates and iron oxides). Mineralogical analyses show a dominance of aluminosilicate clay minerals (kaolinite) with minor fractions of iron oxides in the clay fraction. The increase in clay with depth can be explained by the highly leached nature of the soils in this area and this high degree of leaching may have a washing effect leading to enhanced clay accumulation in the lower horizons. It is worth noting that in some highly leached soils (Oxisols) clay content doesn't necessarily increase with depth. The clay mineralogy is also characteristic of soils formed from prolonged natural weathering processes. Ulrich and Sumner (1991) report that kaolinite, aluminium oxides and iron oxide rich clay minerals dominate the clay fraction of acid soils that develop from natural processes of

acidification. Figures 4.5-4.8 are XRD scans of the clay fraction of representative soil profiles (layers) studied. Kaolinite dominates as the major mineral in all the profiles studied with minor phases of quartz, mica and iron oxides (goethite, hematite). The mineralogy remained essentially the same within different soil horizons from the topsoil to the lower soil horizon in all the profiles studied.

5.2 Major elements

Parent material can exert a great influence on the elemental composition, mineralogy and particle size in soils (McBride, 1994). This property is observed for site A10 having a higher MnO, MgO, CaO, and Na_2O content compared to the other sites. This soil profile developed on a dolerite dyke (a mafic igneous rock) whereas other soils develop on sedimentary rocks. Samples A3, A4, A5 and A17 have a higher K_2O content than the other samples. A3 is underlain by basalt and andesite while A4 and A5 are underlain by shale. Buhmann (1986) reports soils in the Highveld formed from different parent materials but having similar chemical properties.

Soil moisture content and loss on ignition were determined and used to correct the major elements analyses since these measurements were done on powder briquettes and not on fusion discs. This procedure ensures complete removal of any organics and eliminates all water in the sample. Soil moisture content was measured using air-dried (< 2 mm) soil. Moisture content was generally higher in the subsoils than in the topsoils. This increase can be attributed to an associated increase in clay content with depth. The LOI shows a reverse trend to that of the soil moisture content, highest in the topsoil and decreasing with depth. Soil organic matter is the major factor controlling LOI and the trend to decrease with depth agrees with decreasing soil organic matter content with depth. Loss on ignition has been used in some studies as an estimate of soil organic matter content. The realisation that water molecules held in the interlayer of clay minerals and water not given off during air drying of the soil also contribute to LOI made this soil property inappropriate as a good estimate of soil organic matter. The general trend of decrease with depth for this soil property agrees with the trend of decreasing organic carbon content (chapter 5.12).

5.3 Major soluble ions

Ionic charge balance exceeded 10% in most of the samples analysed. The principle of charge balance dictates that in an electrically neutral solution the total concentration of cation charge must equal the total concentration of anion charge (Reuss and Johnson, 1986 and Drever, 1997). Total cation concentration in all cases exceeded total anion concentration. Reasons for the charge imbalance are probably because dissolved organic matter (considered to be predominantly negatively charged in soils) and alkalinity (bicarbonate) were not taken into account in the charge balance calculations. The sum of both anions and cations correlated well with the electrical conductivity (EC) of the saturated paste extracts. The EC increased with increasing ionic strength of the soil solution.

5.3.1 Major anions

The average concentration of soluble anions decreases according to the following order: SO_4^{2-}>Cl^-> NO_3^-. The concentration of SO_4^{2-} and chloride shows similar patterns in most soil profiles studied with maximum concentration occurring in the topsoil (0-10 cm) and decreasing with depth. This decrease was matched by a corresponding decrease in the electrical conductivity of the saturated paste extracts with depth. Nitrate shows a different trend from that observed for Cl^- and SO_4^{2-} (Figure 5.1). It suffices to say that soluble nitrate is the most readily available nitrogen source to plants and therefore probably taken up by plants in the topsoil. The concentration may therefore be higher in lower soil horizon not reached by shallow vegetation root. Plants and microorganisms (bacteria) in the topsoil may speed up the process of denitrification leading to lower concentrations of nitrate in the topsoil.

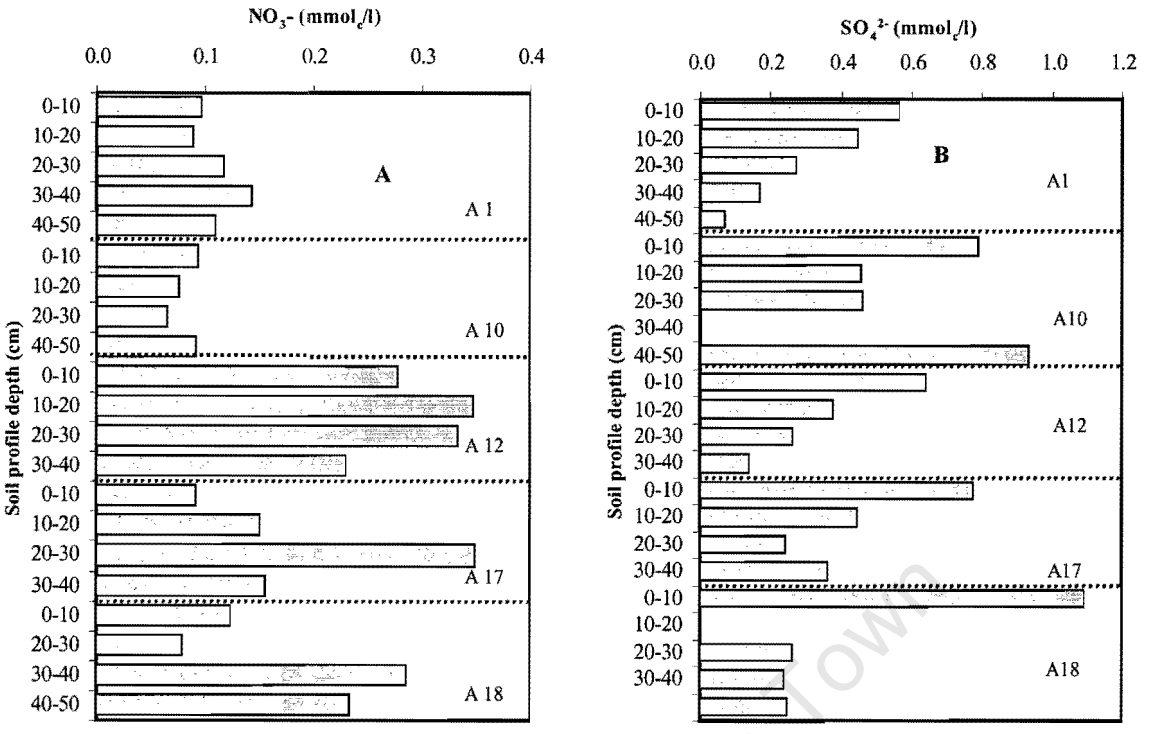


Figure 5.1 Change in concentration of soluble nitrate (A) and sulfate (B) with depth for 5 soil profiles.

Van Tienhoven (1997) reported that the highest concentration of soluble sulfate in saturated paste extracts occurred within 4-6 km of radius from the power station in the direction of sampling (downwind in the prevailing wind direction). In order to confirm whether this increase was influenced by atmospheric input from the power station, the sampling density was increased within 2-6 km distance from the power station. Two additional samples were collected within this distance. Another two additional samples were collected 6 km north and south of the power station (A18 and A19, respectively) to find out whether this increase was from a local source or was a result of regional input from the greater industrial Highveld region.

Soluble sulfate in saturated paste extracts (SPE) show some similarity to earlier results obtained in 1997. The highest concentration of soluble sulfate occurred at site A16 located some 3 km from Arnot power station in the ENE to SE transect. Similar concentrations obtained for site A12 in the previous study were obtained in the current study. The results conform to pollution dispersion modelling results done on some power stations in the Highveld. Turner *et al.* 1996 report plume strikes as close as two stack heights from the point

source but say that the average position for maximum impact is about ten stack lengths downwind from the source. The emission stacks at Arnot are about 200 m in height.

5.3.2 Major cations

The following cations (Na^+, K^+, Ca^{2+}, Mg^{2+} and NH_4^+) were determined in SPE and the following order of dominance was observed Ca^{2+}> Mg^{2+}> K^+> NH_4^+>Na^+. Calcium was the dominant cation in SPE for a majority of the profiles with Mg and K dominating in a few. The topsoils (0-10 cm) are enriched in most of the cations relative to the lower soil horizons. No apparent trend of increasing or decreasing concentration of cations with distance from the power station was observed. Sites A10 and A18 show higher concentrations of Ca than the rest of the profiles. Atmospheric deposition of sulfur has been reported to be associated with basic cations such as Ca, Mg and K (Reuss and Johnson, 1996).

5.4 Cation exchange capacity

The cation exchange capacity (CEC) was estimated as the sum of the exchangeable base cations (Ca and Mg) and the extractable acidity.

CEC = [Ca]+[Mg]+[exchangeable acidity], the brackets represent the concentrations in $mmol_c/kg$ soil.

The CEC ranges between 20.5 and 51.6 $mmol_c/kg$ in the 2000 samples. The CEC is highest in the topsoils and decreases with depth. In some sites for example A1 and A18, the CEC drops by about half the value in the topsoil down to the lower soil horizon. Maximum CEC occurs in soil horizons with higher organic matter content. It is evident from the results that the organic matter exerts a greater control on CEC than the clay content of the soils.

5.5 Soil pH

An hypothesis of this study is that soil acidity might be increasing as a result of increasing atmospheric deposition of sulfur. Figure 4.1 shows the relationship between soil pH measured in 1 M KCl and the pH measured in distilled water. According to Alloway (1995), pH measurement of the supernatant of a soil/H_2O mixture gives values that are 1 to 1.5 units higher than that of the soil solution near the solid surfaces. This is because H^+ ions are capable of replacing other cations on exchange surfaces thus reducing the activity of H^+ in the supernatant and concentrating the protons in a diffuse layer near the soil surface. It is expected that a sample with a higher cation exchange capacity would have a greater ΔpH_{KCl} because there are more exchange sites on which the H^+ ions can be replaced by other cations.

ΔpH KCl here refers to the difference between the pH in distilled water and pH in 1 M KCl solution.

The elevated values of pH measured in saturated paste extracts relative to that taken in distilled H_2O and 1M KCl may be due in part to the degassing of CO_2, which results from the suction during extraction. Increases in soil pH resulting from degassing of CO_2 during collection of soil water have been reported by Blaser *et al.*(1999). Another factor that may contribute to the elevated pH of saturated pastes could be the longer equilibration time, 24 hours compared to about a quarter of an hour for KCl and H_2O equilibration. The longer equilibration time could enhance the dilution effect (more H^+ ions to going into solution with a longer equilibration time).

pH shows no distinctive trend with distance from the power station. Within a distance of 1.3–5.5 km from the power station, the pH was slightly lower compared to the other profiles. Soil profile A2 which is located 16.9 km from the power station also registered pH values similar to those of the soil profiles within the 1.3–5.5 km distance.

The drop in pH with depth can be attributed to increasing clay content down the soil profiles and the associated increase in the concentration of exchangeable H^+ and Al^{3+} ions. During equilibration of the soil more H^+ gets released into solution in the lower horizons (more clay rich) and hence these samples have lower pH values. Hydrolysis of Al^{3+} will also release H^+ into solution. Drever (1997) holds that the pH of a soil solution is related to the exchangeable H^+ ions on soil surfaces, the hydrolysis of exchangeable aluminium and sometimes the dissociation of carboxylic acid groups on organic matter.

Soil pH shows no significant change between the years, 1996 and 1999 (Figure 5.2). The pH stayed more or less the same with slight changes that may be attributed to spatial variability in the field or change due to analytical uncertainty. In Figure 5.2 the points plot more or less, equally above and below the equivalence line. Due to the different sampling adopted in 2000, it is difficult to directly compare the pH results with those of earlier samples. But the results of pH obtained in 2000 fall within the range of earlier samples despite the difference in sample collection. McBride (1994) report the role of aluminium in buffering soil pH between 4.5 and 5. With increasing proton input to the system, aluminium clays will dissolve and releasing Al^{3+}. Each mole of Al^{3+} produced is capable of releasing three moles of acidity through hydrolysis. The weathering of kaolinite for example can be illustrated by the following reaction:

$Al_2Si_2O_5(OH)4\ (s) + 6H^+(aq) \rightarrow 2Al^{3+}(aq) + 2H_4SiO^o_4(aq) + H_2O(l)$.

Kaolinite weathering consumes H^+ ions according to the above reaction and releases Al^{3+}. Soil pH can be buffered by the above reaction due to the consumption of H^+ ions.

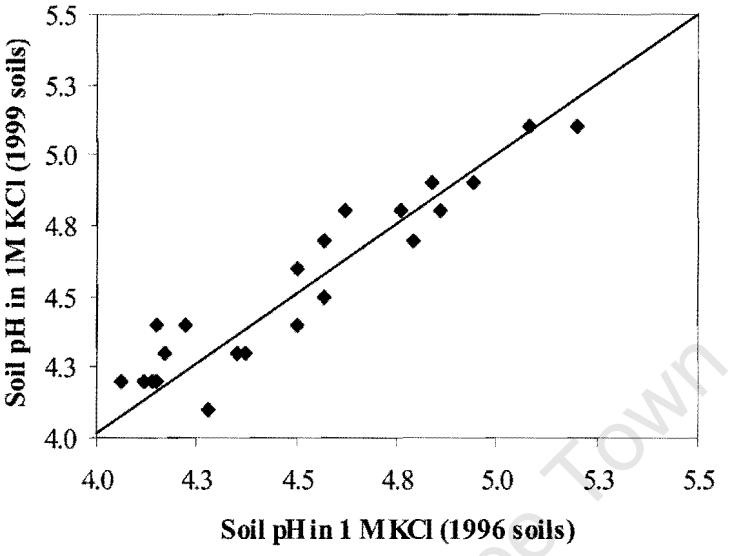


Figure 5.2 Comparison of soil pH measured in 1M KCl solution for soils collected in 1996 and in 1999 form the same area (data from Fey *et al.*, 1999a)

5.6 KCl extractable acidity

Extractable or exchangeable acidity refers to the acidity associated with the solid phase of soils that can be displaced with a concentrated neutral salt. This acidity consists of bound H^+ associated with easily dissociating carboxylic acid groups as well as phenolic groups on humus, organically bound Al^{3+}, and H^+ and Al^{3+} occupying cation exchange sites (Sposito, 1989; McBride, 1994). Extractable acidity is an important property of soils because it gives an indication of the amount of reserve acidity. This reserve pool of acidity in soils is an important consideration when liming.

Extractable acidity has a mean concentration of 6.3 $mmol_c/kg$ (n=29) and ranges from 1 to about 14 $mmol_c/kg$. There is an increase in extractable acidity with depth in all the profiles studied (Figure 4.3) and this correlates negatively with soil pH (pH decreases with depth as mentioned in chapter 4.1). Higher extractable acidity was obtained for samples with lower pH. The relationship between soil pH in KCl and extractable acidity is plotted in Figure 5.3.

Extractable acidity also correlates with clay content. Particle size analysis shows an increase in clay content with soil profile depth and this suggests a greater pool of exchangeable Al^{3+}

and H^+ in the clay-rich sections of the soil profile. Acidity, even though correlated with clay content, was not directly proportional to the amount of clay. Sample A18 (20-30 cm) for example with about twice as much clay as sample A12 (20-30 cm) had only 1 $mmol_c/kg$ of acidity while the latter had 13 times more acidity. This suggests that, although clay content exerts control on the extractable acidity, other factors are equally important. Sample A12 is located 5.5 km downwind of the power station and falls within the area suspected to be receiving the highest input of atmospheric deposition from the power station whereas sample A18 is located about 6 km north of the power station.

Figure 4.3 shows the increase in extractable acidity with depth for selected soil profiles. The increase of exchangeable acidity with depth may be due in part to an increase in negatively charged clay adsorption sites in the lower soil horizons. Since organic matter studies show that there is more organic matter accumulation in the topsoil than in the subsoil, it is unlikely that this exchangeable pool of acidity can be related to soil organic matter. Nevertheless carboxylic acid groups associated with the soluble humus fraction can contribute to the exchangeable pool of acidity in the subsoils.

The ratio of extractable acidity to effective cation exchange capacity is plotted against pH in KCl in Figure 5.4 and the data agrees with the classical relationship between acid saturation of the exchange sites and soil pH (Sposito, 1989, p. 214). Van Tienhoven (1997) found a similar relationship with the soils around Arnot.

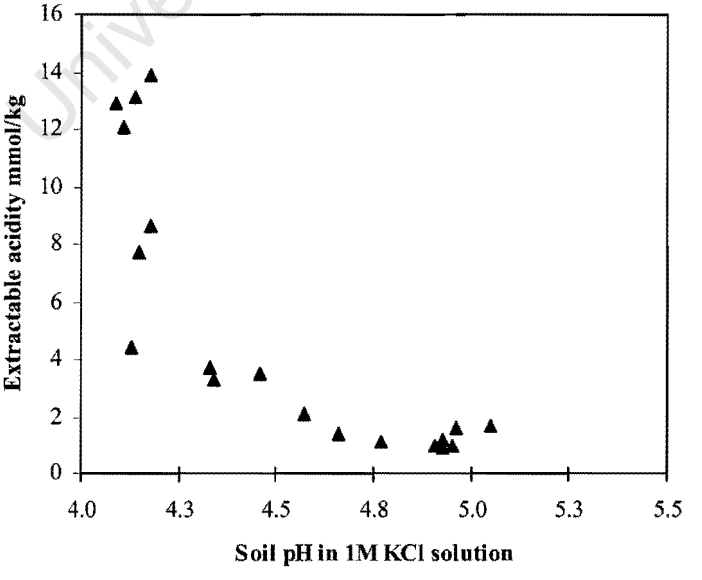


Figure 5.3 Relationship between KCl extractable acidity and soil pH measured in 1M KCl solution.

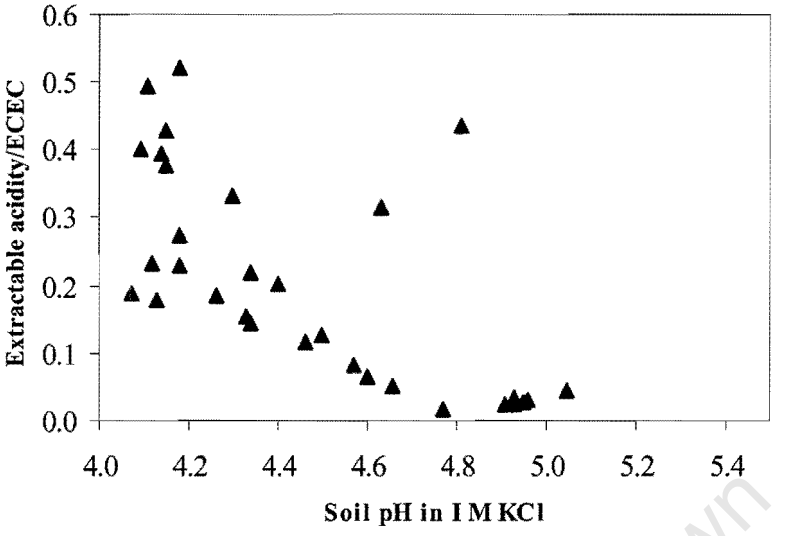


Figure 5.4 The relationship between the acid saturation of the effective cation exchange capacity (ECEC) and pH measured in 1 M KCl.

5.7 Extractable base cations

Organic carbon was found to correlate with extractable base cations (Ca and Mg) in all soil samples (Figure 5.5 shows a plot of extractable Ca and organic matter for selected soil profiles). Magnesium shows a similar relationship with organic carbon. Organic matter has been reported as being able to provide the largest pool of macronutrients in soils because of its ability to enhance retention of cations (high cation exchange capacity), for example Al^{3+}, Fe^{2+}, Ca^{2+}, Mg^{2+}, and NH_4^+ (Baldock and Nelson, 2000).

Sample A4 with the highest organic carbon content in the topsoil (2%) recorded the highest concentration of exchangeable Ca and Mg. By contrast, site A19 with the lowest concentration of organic carbon in the topsoil, registered a relatively low amount of exchangeable base cations. The high negative charge associated with humic substances can provide adsorption sites for positively charged cations. Calcium and magnesium are important nutrients released during the breakdown of soil organic matter.

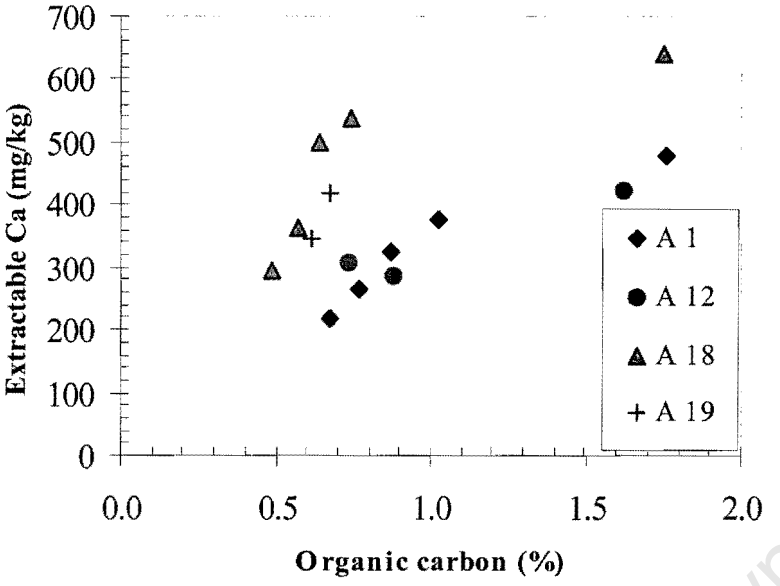


Figure 5.5 Relationship between soil organic carbon and exchangeable base cations (Ca).

5.8 Base saturation

The negative charge associated with clays and humic substances is balanced by cations that exist on clay exchange sites. These cations can be basic (Ca^{2+}, Mg^{2+}, K^{+} and Na^{+}) or acidic (H^{+}, Al^{3+}, $AlOH^{2+}$ or $Al(OH)_2^{+}$). Base saturation refers to the percentage of cation exchange sites occupied by basic cations. For this study only Mg^{2+} and Ca^{2+} have been used to represent the base cation suite. The base saturation in this report is therefore only an estimate and there is a possibility that other constituents (Na^{+} and K^{+}) may contribute to the actual base saturation. Calcium and magnesium generally dominate the exchangeable base cations in acid soils (M. V. Fey, pers. comm. 2000).

Base saturation was calculated by dividing the sum of the base cations (Ca and Mg) by the cation exchange capacity (CEC) and multiplying by 100. It is reported as a percentage.

Base saturation results were similar for 1996 and 1999 soils. Both years showed no change in the base status of the soils. Average base saturation for 1996 was about 84% and that for 1999 was about 83%. Topsoils had higher base saturation than subsoils in most cases. Base saturation showed no clear trends with distance from the power station.

There is about a 6% difference between the base saturation in 2000 samples and those obtained in 1996 and 1999. Average base saturation dropped to 78% in 2000. The contrast

may be due to the different sampling strategy adopted in 2000. Soil samples were collected in some cases at slightly greater depths (up to 50 cm in some profiles). Base cation concentration deceased with depth in the soil profiles. Sampling at slightly greater depths can influence base saturation results as observed. The change of this variable with depth for the 2000 samples was also interesting. The base saturation shows abrupt changes beyond certain depths in the soil profile. For example, in soil profile A1 base saturation dropped from 93.5% in the topsoil (0 – 10 cm) to 53.7% in the lower horizon (40 – 50 cm) while a drop from about 98.4% in topsoil to 56.6% just 20 cm lower in the profile was observed in sample A4.

Base saturation results are consistent with the greater extractable acidity in the lower soil horizons. Higher base saturation is observed for the top horizons and lower base saturation for the deeper soil horizons. What this suggests is that cation exchange sites in the lower soil horizons are dominated by acid cations, which is in conformity with the greater extractable acidity in the subsoils. By extension, the acid saturation of the samples is also consistently lower in the 1996 and 1999 samples compared to the 2000 samples. Figure 5.6 shows the relationship between base saturation and soil pH in 1 M KCl. The base saturation increases with increasing soil pH.

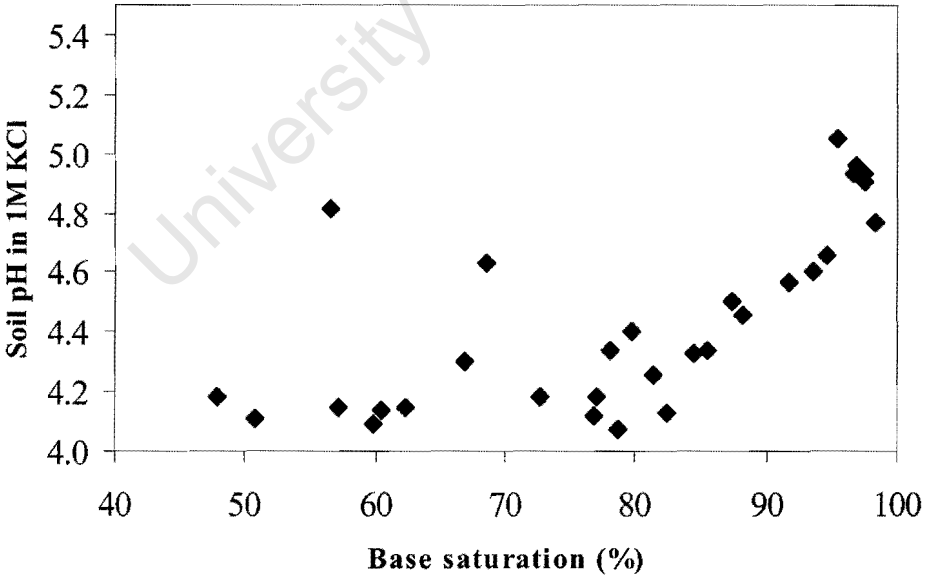


Figure 5.6 Relationship between soil pH measured in 1 M KCl solution and base saturation.

Kuylenstierna (1996) speculated that the input of base cations from soil dust and industrial emissions could be a possible explanation for the high base saturation existing in the upper horizon of these highly weathered acidic soils in the ETH. The industrial Highveld region is a major coal-producing region in South Africa. A lot of mining activity is also carried out in this region. Rock blasting may generate nutrient rich dust, which can contribute to the high base saturation on the soil surface. Industrial emissions have also been reported to contribute to input of base cations in soils (Reuss and Johnson, 1986).

In low rainfall areas, where leaching is very low, accumulation of base cations can take place on the surface. Schloemann (1994) reported the input of base cations to the soil surface as a result of capillary action where the dominant movement of water in the soil is to the surface and where rates of evaporation exceed rates of rainfall thereby enriching the surface with base cations and depleting the subsoil. This might the case in the ETH region only in winter when rainfall is low. In summer high rainfall episodes are registered that can have a high leaching effect.

Nutrient cycling by plants may also contribute in part to the enrichment of base cations in the upper soil horizons. An enrichment of base cations can occur in deep saprolitic zones due to incomplete weathering and also an accumulation by leaching from above. Uptake from these deeper zones of enrichment and redeposition of bases at the surface by plants (phytocycling) can enrich the surface soils with base cations. Base cations can be stored at the surface on cation exchange sites associated with humus in the topsoil. The weathered subsoil rich in kaolinite and iron oxides has low cation exchange capacity compared to organic matter rich topsoil and so cations tend to leach readily from this part of the profile.

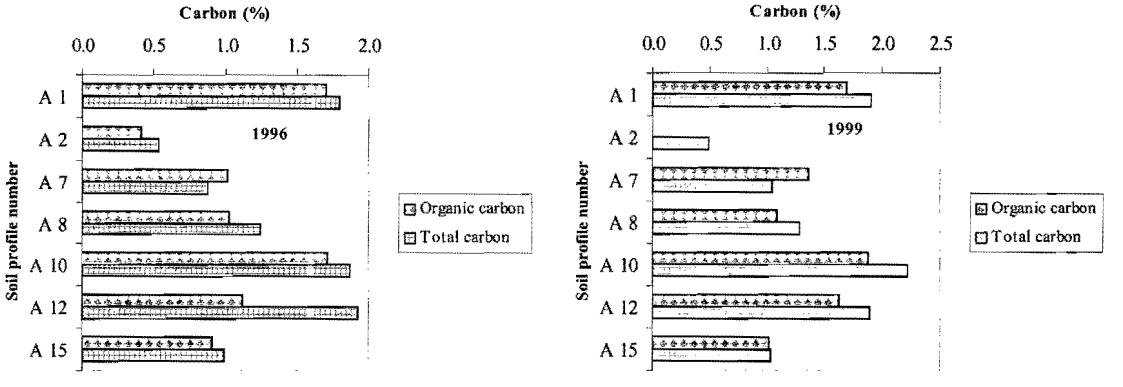
5.9 Comparisons of methods employed in carbon analyses

The results obtained for soil organic carbon analyses by hot digestion and colorimetric method were compared with results obtained for organic carbon analysis by the Walkley Black (wet oxidation) technique (Tables 5.1 and 5.2). The Walkley Black technique was employed to quantify OC content in the 1996 and 1999 soils (Van Tienhoven, 1997; Fey *et al.*, 1999). The results show that the Walkley Black method tends to overestimate the organic carbon content of the soils by about 0.5 wt %. This, therefore, suggests that the average correction factor of 1.3 used in the calculation might not be suitable for soils from this area. In the Walkley Black wet oxidation method where no external heat is applied, it is assumed there is incomplete oxidation of all carbon in the soil and a recovery factor of 1.3 is applied to

correct for this incomplete oxidation. This factor of 1.3 is considered suitable for use in calculating organic carbon content across different soil types. Olanyinka *et al.* (1998) showed that the average correction factor of 1.3 used in the calculation of soil organic carbon overestimates soil organic carbon content for some Nigerian soils. Higher estimates of organic carbon may also result from interference due to the presence of Fe^{2+} and Cl^- in the sample during titration (Baldock and Nelson, 2000). This is unlikely in these well oxidized and non saline soils.

Using total carbon results as a standard, the hot digestion/colorimetric technique used in this study appears to give a better estimate of soil organic carbon when compared to the Walkley Black method. The colorimetric method as indicated above, involves controlled heating of the samples to oxidize completely all the carbon present and because of this heating, no correction factor is applied.

Total carbon analysis gave similar results to those obtained for organic carbon by colorimetry (Figure 5.7). Total carbon content was slightly higher in most cases than organic carbon. The average difference between the two was about 12% but in sample A12 the difference was about 30%. Since these soils are highly leached and acidic with pH < 5 it is assumed that soil carbon is essentially organic. Carbonates minerals are not expected and XRD analyses of the clay size fraction (chapter 4) show no carbonate minerals present. The slight difference between total carbon and organic carbon results may be a result of the incomplete oxidation of carbon in the samples despite the heat applied. The colorimetric method can be used for purposes of comparison and the total carbon method for actual carbon content of the soils. These two methods are therefore recommended for future work on soils from this area.



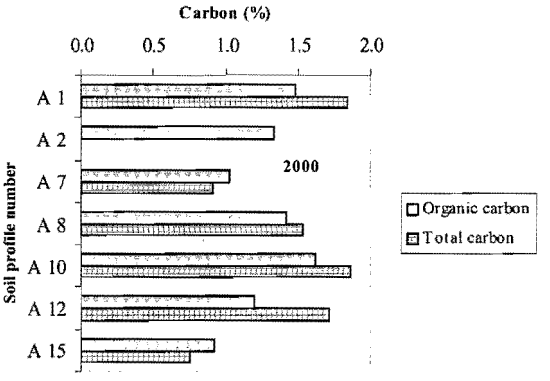


Figure 5.7 Comparison of total carbon and organic carbon for three sets of soils collected from the same area and analysed by the same methods. (OC was analysed by the colorimetric method)

Table 5.1 Organic carbon data for soils collected in 1996 and analysed by the Walkley Black wet oxidation method (WB) and the colorimetric method involving heating (HM) (WB data from Fey *et al.*, 1999a).

Topsoils	Dist from PS	96 HM	OC 1996 WB	Mean	SD
1	19.9	1.70	1.64	1.67	0.03
4	12.8	1.49	2.47	1.98	0.49
5	10.7	1.92	2.36	2.14	0.22
6	1.3	1.27	1.55	1.41	0.14
7	8.1	1.02	1.18	1.10	0.08
8	14.4	1.03	1.25	1.14	0.11
10	8.3	1.72	2.17	1.94	0.23
11	4.5	0.89	1.36	1.13	0.23
13	5.8	0.60	1.10	0.85	0.25
15	1	0.91	0.88	0.89	0.01
Subsoils					
3	14.8	0.38	0.81	0.60	0.21
4	12.8	0.80	1.36	1.08	0.28
7	8.1	0.48	1.29	0.89	0.40
8	14.4	0.43	0.74	0.59	0.15
9	12.6	0.64	0.88	0.76	0.12
12	5.5	0.65	0.88	0.76	0.12
14	18.8	0.37	0.40	0.39	0.01
15	1	0.54	0.59	0.56	0.03

Table 5.2 Organic carbon data for soils collected in 1999 and analysed by the Walkley Black wet oxidation method (WB) and the colorimetric method involving heating (HM) (WB data from Fey *et al.*, 1999a).

Topsoil	Dist. From P S	1999 HM	1999 WB	Mean	SD
1	19.9	1.70	2.18	1.94	0.24
2	16.9	1.41	1.65	1.53	0.12
3	14.8	0.85	1.09	0.97	0.12
5	10.7	1.68	2.60	2.14	0.46
6	1.3	1.41	1.74	1.58	0.16
7	8.1	1.36	2.11	1.73	0.38
8	14.4	1.08	1.82	1.45	0.37
9	12.6	1.33	2.59	1.96	0.63
10	8.3	1.88	3.20	2.54	0.66
11	4.5	0.95	1.94	1.44	0.50
12	5.5	1.62	2.38	2.00	0.38
14	18.8	0.62	1.10	0.86	0.24
15	1	1.02	1.28	1.15	0.13
Subsoils					
1	19.9	0.85	1.61	1.23	0.38
3	14.8	0.68	0.54	0.61	0.07
4	12.8	0.81	1.61	1.21	0.40
5	10.7	1.01	0.99	1.00	0.01
6	1.3	0.78	1.15	0.96	0.19
7	8.1	0.52	0.84	0.68	0.16
8	14.4	0.46	1.03	0.75	0.28
9	12.6	0.65	1.18	0.91	0.27
11	4.5	0.47	0.73	0.60	0.13
12	5.5	0.58	1.11	0.85	0.26
13	5.8	0.35	0.69	0.52	0.17
14	18.8	0.52	0.54	0.53	0.01
15	1	0.44	0.88	0.66	0.22

5.10 Organic carbon

An hypothesis of this study is that organic matter accumulation has increased in the soils around Arnot power station as a result of increased atmospheric deposition of pollutants to the soil.

Lukina and Nikonov (1998) report an increase in organic carbon in the soils from northern Taiga Al-Fe-humus podzolic soils. They attributed this increase to increased deposition of atmospheric pollutants. Their assertion was that increase atmospheric deposition would lead to increase litter fall and a build up of organic matter in the soil as well as formation of humus from dead roots of plants in the soil. An accumulation of soil organic matter near a copper smelter in Zambia was reported by Chishala *et al.* (1997). They claimed that due to the low

pH of the soils around the smelters organic matter decomposition is low and consequently there is a build up of OM in the soils.

An increase in soil organic carbon of 32% from 0.558 wt % to 0.738 wt % within a period of 5 years was reported for soils in the Pretoria area (Theron, 1961). Fey *et al.* (1999a) report a possible increase in organic carbon in the soils around Arnot power station as a result of increasing atmospheric deposition. The present study was undertaken in part to obtain greater clarity on whether this assertion is true or if the likely increase reported by Fey *et al.* (1999a), was within analytical uncertainties.

Organic carbon results show that the topsoils (0-10 cm) are enriched in organic carbon relative to the lower horizons in all profiles studied. A sharp decline of the organic carbon beneath 10 cm in all profiles is apparent.

The decline in soil organic carbon below 10 cm depth in most profiles may be explained by the fact that soil organic matter accumulation is only taking place at the soil surface. The results clearly differentiate between topsoils and subsoils based on their organic carbon content.

A comparison of the organic carbon content for soils collected in 1996 and 1999 shows an average increase of about 11% for the entire soil collection. There was a significant increase in five out of the 21 samples used in the comparison and a significant decrease in one sample (Figure 5.8). The rest of the samples plot equally above and below the equivalence line to an extent dictated only by spatial variability effects in the field.

In formulating the hypothesis that organic matter accumulation in the soils around Arnot might be increasing, it was speculated that: sulfur and perhaps nitrogen enrichment from atmospheric deposition provides these elements as nutrients to microorganisms (bacteria) which feed on organic residues and if sulfur is in limited supply, then enrichment will enhance microbial biomass and ultimately the amount of humus that is formed from plant residues. Conversely if sulfur is in short supply, then much of the carbon will be evolved as CO_2 during microbial breakdown.

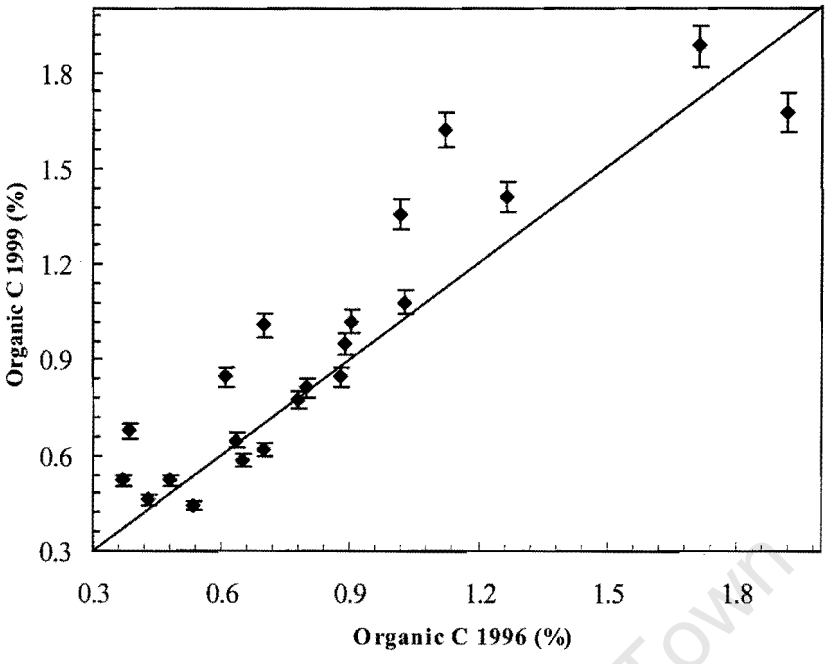


Figure 5.8 Comparison of organic carbon for soils sampled in 1996 and in 1999 analysed using the colorimetric method.

Sulfur from atmospheric deposition is not only deposited as SO_4^{2-}, it is associated with H^+ ions, which can increase soil acidity. An increase in soil acidity may suppress the activity of soil microbes involved in the breakdown of soil organic matter (Cresser *et al.*, 1989). If sulfur deposition results in a lower soil pH, then it may aid in the biological stabilization of organic matter against processes of decomposition. The fact that soil pH remained essentially the same in all three sets of samples with no significant change suggests that this is not the case with the soils around Arnot. In moderately to strongly acid soils (pH< 5.5), the role of aluminium in buffering soil pH becomes very important and this will delay the translation of H^+ inputs into active or measurable acidity (chapter 5.7).

This hypothesis that organic matter may be accumulating as a result of increased atmospheric deposition of pollutants (S) to the soil, can be tested in future work by conducting laboratory experiments using a decomposing carbon source to see what happens upon addition of sulfur and or nitrogen to the system.

Increased atmospheric deposition of pollutant gases (mainly SO_2) would initially supply the soil with macronutrients (S, N) and major base cations Ca and Mg needed for plant growth. This supply of nutrients will enhance biomass production. An increase in biomass production

will therefore enhance soil organic matter accumulation. Sulfur is an important macronutrient for plant growth and can limit plant growth in sulfur-poor soils (Buckman and Brady, 1969). Grobler *et al.* (1999) have anticipated a decrease in sulfur in some South African soils (remote from air pollution sources) as a result of the manufacturing of higher-grade fertilizers applied to these soils, from material poor in sulfur. Meyer *et al.* (1971) have reported sulfur deficiency as limiting the growth of sugar canes in sulfur poor soils in South Africa. No such danger has been reported by farmers in the ETH region.

5.11 Soil sulfur

Soil sulfur exists in a variety of organic and inorganic forms and oxidation states, and is involved in a variety of chemical and biological reactions, and interacts with the lithosphere, hydrosphere and atmosphere either naturally or as a result of human interference (Freney and Williams, 1983). In well-drained, well-aerated soils, inorganic sulfur is almost entirely in the form of sulfates. Sulfate-sulfur commonly increases with depth in a soil profile. Tabatabai (1987) reports that inorganic sulfur accounts for < 5% of the total sulfur in most soils from humid and semi-humid regions. Sulfate in soils can occur as water-soluble salts, adsorbed by soil colloids, or as insoluble forms. Sulfides and other sulfur compounds with sulfur in lower oxidation states than in SO_4^{2-}, including elemental sulfur, can form under anaerobic conditions such as occur in tidal swamps and waterlogged soils (Starkey, 1966).

The three pools of sulfur in soils around Arnot namely soluble sulfur, adsorbed sulfur and organic sulfur have been looked at separately. These fractions all make up total sulfur. Soluble sulfur has been looked at in the discussion on soluble anions in saturated paste extracts and will also be considered later on in a discussion on the pools of sulfur (chapter 5.15). Total sulfur will be looked at in the next section in a discussion on the relationship between sulfur and organic carbon.

5.11.1 Adsorbed (extractable) sulfate

Adsorbed sulfate is important in the study of soil acidification (Singh, 1982). Tabatabai (1987) reviewed the following factors controlling the adsorption of sulfate in soils:

i. *Clay content and type of clay mineral.* Sulfate adsorption usually increases with increasing clay content of the soils. Some clay minerals will retain more sulfate than others. The capacities of hydrogen saturated clays for SO_4^{2-} adsorption are kaolinite> illite> bentonite with adsorption about equal for illite and kaolinite when clay is saturated with Al.

ii. *Hydrous oxides (variable charged minerals).* Hydrous oxides of Al and to a lesser extent of Fe show marked tendencies towards the adsorption of SO_4^{2-} and these compounds are responsible for the bulk of SO_4^{2-} adsorbed in many soils.

iii. *Soil horizon or depth.* It has been shown that most soils have some capacity to absorb SO_4^{2-} but this capacity is often greater in the lower soil horizon. This is probably due to the presence of more clay and iron oxides and less organic matter in these lower horizons (except in spodosols).

iv. *Effect of soil pH.* pH controls the adsorption of SO_4^{2-} in soils: adsorption is higher at low pH and becomes almost negligible above pH 6.

v. *Sulfate concentration and temperature.* Concentration and temperature control the amount of SO_4^{2-} adsorbed. Adsorbed SO_4^{2-} is in kinetic equilibrium with SO_4^{2-} in solution.

vi. *Effect of time.* The adsorption will increase with the length of time SO_4^{2-} is in contact with the adsorbing substance.

vii. *Presence of other anions.* The presence of other anions may influence the amount of sulfate adsorbed. In a soup of anions, the strength of retention will decrease with hydroxyl> phosphate> sulfate= acetate> nitrate= chloride.

An enrichment of adsorbed sulfate was observed in the lower horizon of profile A1 a red sesquioxide rich soil (Figure 5.9, A1). Red and yellow Ultisols and Oxisols possess a net positive charge (anion exchange at depth), the magnitude of this charge depending on both the pH and ionic strength of the soil solution (Fey *et al.,* 1990). The higher iron and aluminium oxide content in the subsoil may contribute to the high sulfate adsorption in the subsoil. At low pH, oxides of iron and aluminium possess positive charge sites for the adsorption of negatively charged ions. The combined scenario of high iron and aluminium oxides, low pH and high clay content in the subsoils are favourable for enhanced sulfate accumulation in the lower horizon of soils. Higher phosphate extractable sulfate could also result from a higher sulfate input to the soil. Sample A19 (a sandy soil) also registered a high concentration of extractable sulfate in the lower horizon (Figure 5.9, A19). This sample had the lowest concentration of total sulfur in the topsoil and soluble sulfate concentration was also low. Site A18 gave contrasting results to those obtained for Sites A1 and A19. The concentration of extractable sulfate was higher in the top horizon than in the lower horizon (Figure 5.9, A18). This result does not conform to results of earlier studies that suggest that adsorbed sulfate

concentration is negatively correlated with organic matter due to the competition between negatively charged organic anions and the SO_4^{2-} anion for positively charged sites on soil particles (van Tienhoven, 1997). It should be noted that soil profile A18 is a deep soil profile and the lower horizons might show a reversal in the concentration of adsorbed sulfate.

Enhanced SO_4^{2-} adsorption in the B-horizon of soils has been reported and is believed to depend on the SO_4^{2-} concentration and pH of the soil (Singh, 1982; Tabatabai, 1987; Fey *et al.*, 1990; Karltun and Gustafsson, 1993; Gustaffsson, 1995).

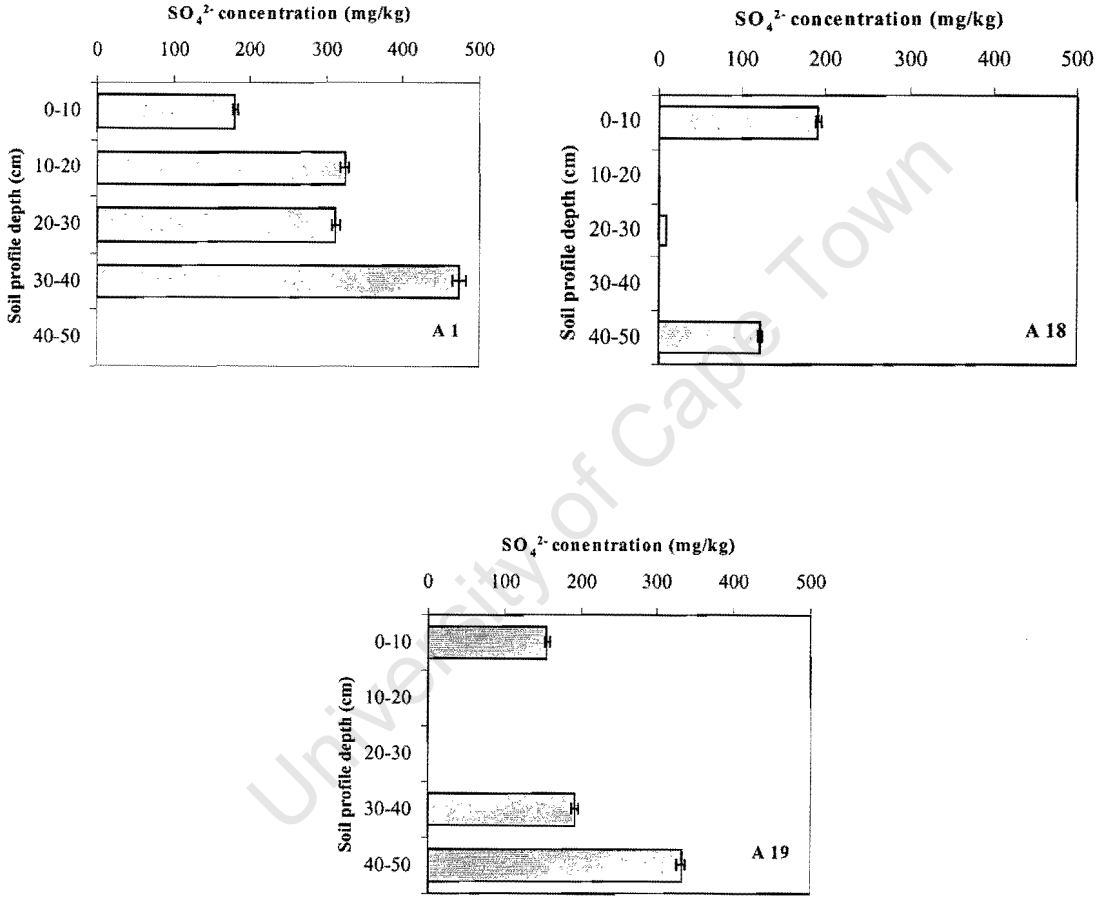


Figure 5.9 Change in extractable sulfate concentration with depth in three soil profiles A1, A18 and A19

5.12 Total sulfur and organic carbon relationships

Total sulfur tends to correlate with organic carbon in all three sets of soil samples obtained in 1996, 1999 and 2000 from the same area (Figs 5.10, 5.11 and 5.12). The sulfur data used for the plots was obtained from van Tienhoven (1997) and Fey *et al.* (1999a) (Table A3 appendix). Organic carbon data are those obtained from analyzing archived 1996 and 1999

samples together with the samples collected in 2000 by the hot digestion/colorimetric method. Sulfur in all three years was analyzed by X-ray fluorescence spectroscopy. There is no significant difference in the linear regression for the three sets of samples (the slopes of the sulfur – carbon relationships remained essentially the same). The slight shift observed for the sulfur – carbon relationship by Fey *et al.* (1999a) might have arisen as a result of the uncertainty associated with organic carbon analyses. The relationship between total sulfur and organic carbon stems from the association of soil sulfur with organic matter.

Rough calculations of the various sulfur fractions show that the bulk of soil sulfur in the topsoil lies in the organic pool with less than 15% being comprised of soluble and adsorbed sulfur (Table 5.3). This agrees with the observation made earlier that sulfur in the topsoil is predominantly associated with organic matter.

The work of Du Toit (1993) confirmed that, for a large collection of South African topsoils, the total sulfur concentration shows a highly significant linear relationship to the organic carbon content. This relationship (i.e. the level of S relative to that of organic matter) has been exploited in many studies e.g. van Tienhoven (1997) and Fey *et al.* (1999a) with the prospect of delimiting areas subject to sulfur deposition. It was speculated that, for a group of soils close to atmospheric emission sources, the intercept of the sulfur-carbon relationship should be greater (reflecting a larger accumulation of inorganic S) than that for soils remote from air pollution sources. It is this concept that has been used to investigate whether accumulation of sulfur could be more intense in the immediate neighbourhood of coal-fired power stations. Van Tienhoven (1997) compared this relationship for soils around Arnot power station with soils from other parts of South Africa remote from any sulfur source. The results showed that background levels were higher at Arnot and other areas receiving sulfur from atmospheric deposition than areas that were remote from atmospheric pollution sources. These results are based on data obtained using different methods of sulfur and carbon analyses. It is difficult to make any conclusions in this study if this is the case. The more recently applied techniques: X-ray fluorescence spectrometry for total sulfur analysis and hot digestion/colorimetry method for organic carbon needs to be employed in analysing soils collected most recently and soils collected a few decades ago from the same area (if available) to better reassess any long-term changes in S and C in these soils.

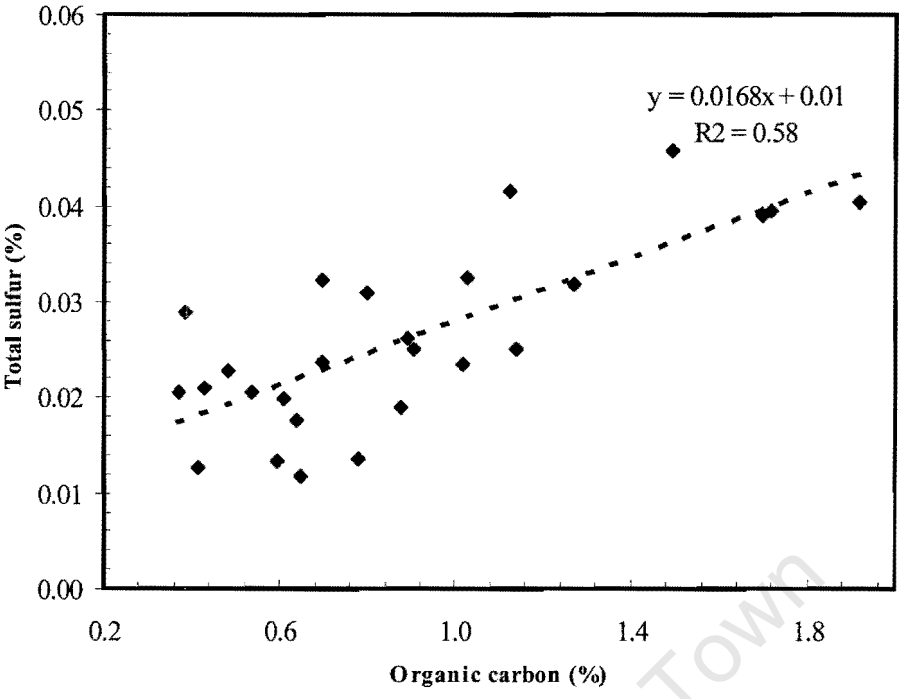


Figure 5.10 Total soil sulfur content in relation to organic matter for soils collected around Arnot power station in 1996.

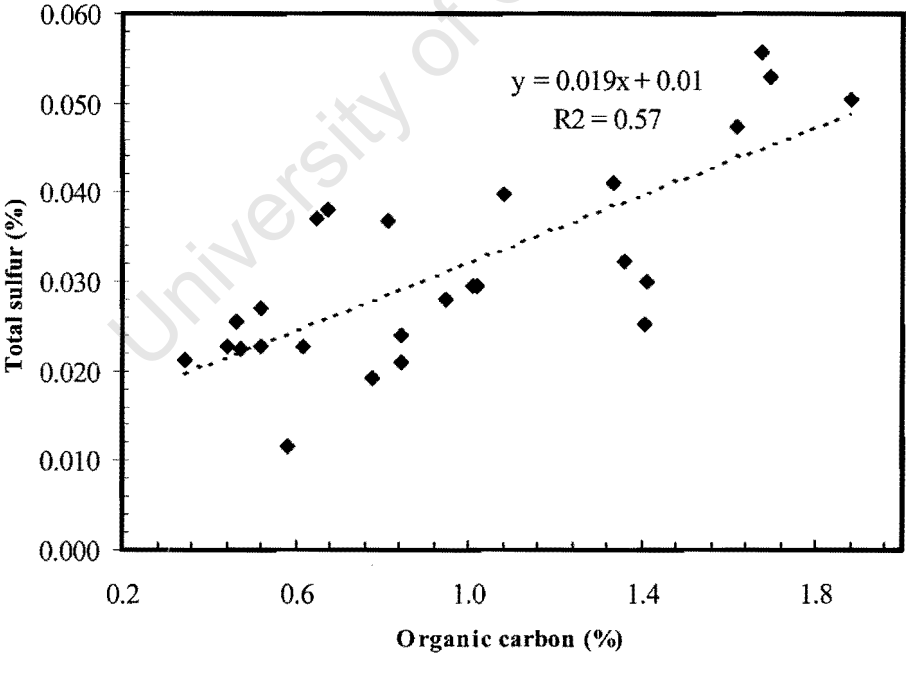


Figure 5.11 Total soil sulfur content in relation to organic matter for soils collected around Arnot power station in 1999.

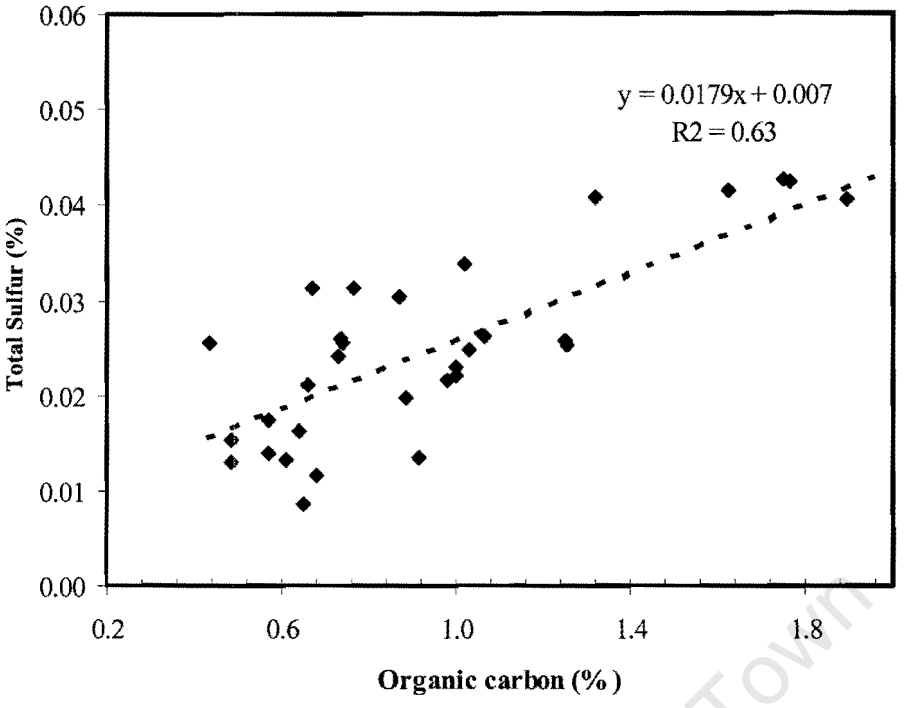


Figure 5.12 Total soil sulfur content in relation to organic matter for soils collected around Arnot power station in 2000.

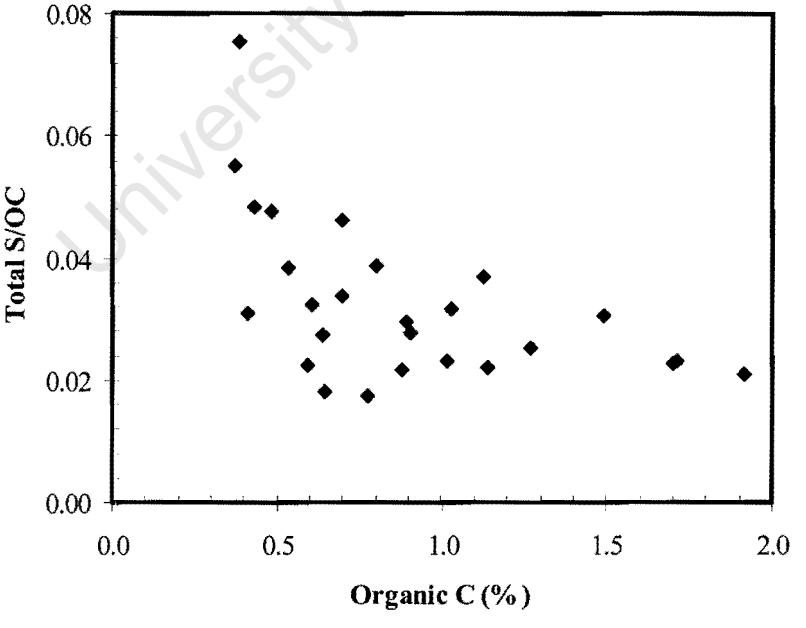


Figure 5.13 The relationship between the ratios of total S/OC to organic carbon for soils collected in 1996.

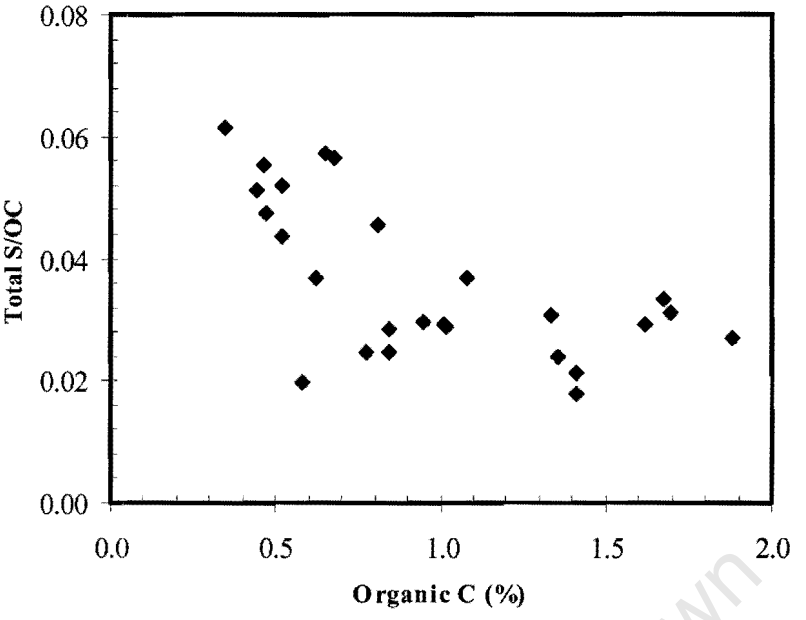


Figure 5.14 The relationship between the ratios of total S/OC to organic carbon for soils collected in 1999.

Figures 5.13 and 5.14 show the relationships between the ratio of total S/OC and OC for soils obtained in 1996 and 1999. The apparent higher total S/OC ratio in the lower organic carbon samples stems from the fact that most of the lower organic carbon samples are subsoil samples where the concentration of adsorbed sulfur is higher. A more uniform relationship is expected when the ratio of organic S/OC is plotted against organic carbon.

5.13 Pools of sulfur in Arnot soils

Some rough calculations were made to access where the bulk of sulfur was accumulating in the soil. Calculations were done only for soils in which complete data of soluble, adsorbed and total sulfur were available (Table 5.3). Soluble sulfur was obtained from sulfate in saturated pastes extracts analysed by ion chromatography while adsorbed sulfate was obtained from phosphate extractable sulfate analysed by ion chromatography. Total sulfur was obtained by XRF analysis. Organic sulfur was derived as the difference between total sulfur and the sum of soluble sulfate and adsorbed sulfate. The ratio of organic sulfur to organic carbon seems fairly constant and has a mean value of 0.02 (Table 5.4). The calculations took into account the amount of soil and solution used in each case (adsorbed and soluble sulfate).

The assumption made here was that since these soils are well aerated, highly leached soils with a reddish brown or reddish colour they are oxidising enough and probably have no

sulfide sulfur in them. It was also assumed that any sulfides present must have been oxidised during air-drying of the samples. From the above it was accepted that no sulfide sulfur would be present in the soils and organic sulfur was estimated as the difference between total sulfur and soluble sulfur plus adsorbed sulfur

In the topsoils, organic sulfur makes up over 80% of total sulfur in most of the soils studied but adsorbed sulfur becomes increasingly important as a sink for sulfur in the lower soil horizons (Table 5.3). Soluble sulfur (sulfate) constitutes a very small sink for sulfur in the entire soil profile. Adsorbed sulfate constituted only about 14 % of total sulfur in the topsoil (0-10 cm) but in the subsoil (30-40 cm depth) adsorbed sulfate increased to about 50 % of total sulfur. Many studies have reported an increase in sulfate adsorption with depth in soils profiles (Gustafsson, 1995). This increase can be matched with an associated increase in clay content, with soil profile depth, increase in iron and aluminium oxides with depth, decrease in pH of the soils with depth as well as with a decrease in organic matter content with depth (Nodwin *et al.*, 1986 and Karltun and Gustafsson, 1993). At lower pH oxides of iron and aluminium posses positive charge (anion exchange capacity) on which negatively charged anions like sulfate can attach (McBride, 1994). Sulfate adsorption has been reported as an important buffering, proton consuming process that acts to delay soil water chemical changes in hydrogen ion concentration (Gustafsson, 1995). This model assumes that for every mole of sulfate adsorbed, two moles of H^+ are consumed.

Microbial degradation of OM results in the release of sulfate that can then adsorb to clay particle surfaces in the lower soil horizon. In this way, there is transfer from organic S to the adsorbed sulfate reservoir with depth in the soil.

Table 5.3 Sinks of sulfur in Arnot soils

Sample	Soluble S (mg/kg)	Adsorbed S (mg/kg)	Total (mg/kg)	Soluble sulfur (%)	Adsorbed sulfur (%)	Organic sulfur (%)
A1 (0-10)	1.0	57.2	424	0.2	13.5	86.3
A 1(10-20)	1.3	9.2	338	0.4	2.7	96.9
A1 (20-30)	0.7	9.3	303	0.2	3.1	96.7
A1 (30-40)	0.9	152.1	311	0.3	48.9	50.8
A4 (0-10)	0.9	41.0	411	0.2	10.0	89.8
A18 (0-10)	0.7	60.9	427	0.2	14.3	85.6
A18 (20-30)	0.6	25.2	161	0.4	15.7	84.0
A18 (40-50)	0.5	38.5	152	0.3	25.3	74.3
A19 (0-10)	0.5	49.5	132	0.4	37.5	62.1
A19 (30-40)	0.0	62.0	114	0.0	54.4	45.6

Table 5.4 Organic sulfur (OS) to organic carbon (OC) ratios.

Sample	OS (mg/kg)	OC (mg/kg)	OS/OC
A1 (0-10)	365.8	18000	0.020
A 1(10-20)	327.5	10000	0.033
A1 (20-30)	293.0	9000	0.033
A1 (30-40)	158.0	8000	0.020
A4 (0-10)	369.2	22000	0.017
A18 (0-10)	365.4	18000	0.020
A18 (20-30)	135.2	6000	0.023
A18 (40-50)	113.0	5000	0.023
A19 (0-10)	82.0	6000	0.014
A19 (30-40)	52.0	7000	0.007

6 GENERAL DISCUSSION AND CONCLUSIONS

Soils in the ETH are inherently acidic, highly leached and lack any carbonate minerals. The soils sampled for this study come from large uncultivated areas implying that the traditional practice of liming is absent and the soils are not subject to any other form of fertilizer application. These soils receive an estimated 30 – 50 kg/ha of sulfur per annum from atmospheric fallout associated with coal-fired power stations (Fey *et al.*, 1999a).

Nineteen soil profiles were sampled from which about 82 soil samples were obtained. Soil pits were dug and soils were collected at intervals of 10 cm from the surface, down to a depth of 50 cm. Due to time constraints, only part of the samples collected were analyzed. The samples selected for analyses were representative of the entire soil collection. The soils were characterized both physically and chemically in the laboratory. Routine soil analyses were carried out on bulk soil as well as on saturated paste extracts. Analyses were done on the bulk sample; air-dried and sieved (< 2 mm). Soil samples collected in 2000 as well as archived samples collected in 1996 and 1999 from the same area were analysed. The 1996 and 1999 samples were used only for certain analyses to which attention will be drawn in the ensuing discussion. The archived samples were all air-dried and sieved (< 2 mm) and stored in plastic sample storage bottles with lids.

To investigate the hypothesis that OC might be accumulating in the soils around Arnot as a result of increased deposition of sulfur from the atmosphere, different methods of carbon analysis were employed on soil samples collected in 2000 and archived soil samples collected in 1996 and 1999 from the same sites. The hot digestion/colorimetric method, which involves heating the sample under controlled temperature for 30 minutes to oxidize completely all carbon present, was employed. The results obtained were used to compare with results obtained by the Walkley Black wet oxidation technique from previous studies. The colorimetric method gave better estimates of the organic carbon content of the soils. The Walkley Black method gave higher estimates of the actual carbon content of the soils. This overestimate was attributed to the usage of a correction factor of 1.3, which is believed to be suitable for use in calculating organic carbon content across different soil types. Total carbon analysis was performed on a selection of samples to serve as a standard in evaluating the hot digestion/colorimetric technique. The results from total carbon analysis were comparable to results obtained by the colorimetric technique. Based on their similar results, it was concluded

that total carbon be interpreted as organic carbon due to the low pH of the soils (< 6) and the absence of any carbonate minerals from XRD analysis of the clay size fraction.

The results suggest a tendency towards a slight increase in organic carbon content in the soils since 1996 but the increase is not significant and falls short of the magnitude speculated by Fey *et al.* (1999a). The entire 2000 soil collection analyzed had broadly similar organic carbon content in the topsoil except for soil profile A19 that had the lowest organic carbon content in the topsoil. This soil profile does not fall in the ENE to SE transect chosen as the most likely area to receive high inputs of deposition from the Arnot power station. With just a single sample, it is difficult to draw any conclusions whether the minimum concentration of organic carbon observed at this site is related to the position of the site relative to the power station or if this difference is as result of some spatial and temporal variation. More samples need to be collected in this direction to see if the organic carbon content is consistently lower.

6.1 Variation in soil properties with depth

Various soil chemical properties show distinct trends with depth in the soil profiles as indicated below:

- The total S content decreases with depth in the same manner as organic C, which confirms the predominantly organic status of S. No apparent trend of increasing or decreasing soil sulfur content with distance from the power station was observed. Organic carbon also showed no definite trend of increase or decrease from the power station.
- Soil pH decreases with depth in the soil profiles and correlates with increasing extractable acidity.
- Extractable base cations decrease with soil depth with the highest concentrations in the topsoil and this also correlates well with extractable acidity that increases with depth.
- Clay content increases with depth and correlates with increasing iron and aluminum oxide contents with depth.
- The cation exchange capacity also increases with depth and correlates with the clay content.
- Soluble ions in saturated paste extracts decrease with depth and correlate well with the electrical conductivity, which also decreases with depth.

6.2 Relationship between soil properties

The relationships between various soil chemical properties are highlighted below.

- Soil organic carbon and total sulfur in all the soil samples studied show a general positive correlation. This relationship results primarily from the sulfur content of organic matter. The uncertainty associated with S and OC analyses might account for the slight shift in the total sulfur-organic carbon relationship reported by Fey *et al.*, (1999a). Initially the accurate estimation of total S was a problem until the wet chemical method formerly used was replaced with X-ray fluorescence spectrometry. After optimising the determination of total sulfur using X-ray fluorescence spectrometry and organic carbon using hot digestion with colorimetric analysis it suffices to say that there is no significant shift so far in the relationship between S and C in the samples collected over a four year period from the Arnot monitoring sites.
- There was a clear relationship between soil pH in 1 M KCl and other soil properties like the base saturation, acid saturation, and KCl extractable acidity.
- The ionic composition of saturated paste extracts also related to the electrical conductivity. The EC increasing with ionic strength of the saturated paste extracts.
- A clear relationship was also observed between KCl extractable acidity and the effective cation exchange capacity.

An estimate of the sinks of sulfur in these soils was made. Rough calculations show that over 80% of total sulfur in the topsoil occurs as organic sulfur with soluble sulfate making up < 1 % of total sulfur and adsorbed sulfur constituting the rest. The organic S/C ratio is fairly constant at a value of 0.02. An appreciable amount of adsorbed sulfur (about 50% of total sulfur) was found in the lower horizon of an iron and aluminum oxide rich soil at site A1. Retention of sulfur in either organic form or as adsorbed sulfur will result in lower fluxes to neighbouring ecosystems. The adsorbed pool of sulfur has important implications in buffering soil acidity and reducing nutrient losses (base cation leaching). Soil retention of sulfur is important and problems associated with elevated sulfur content can continue even after a drop in pollutant emission and deposition, as observed recently in Europe and North America. Quantifying the adsorbed pool of sulfur is therefore important in predicting the recovery time of acidified soils.

Soil pH shows no change since 1996. The observation made by van Tienhoven (1997) that the concentration of water-soluble sulfate had its maximum (13.6-15.6 mg/kg) within 4-6 km of the power station was confirmed. It has been shown that this maximum occurs even closer than speculated at 3 km (36 mg/kg) from the power station. The concentrations of water-soluble sulfate between the 4-6 km distance obtained in this study, are similar to those obtained by van Tienhoven (1997). Reuss and Johnson (1986) report that biological processes and the capacity of soils to retain sulfate can complicate increases in sulfate concentration in soil. The soils within 3 km of the power station where a maximum of soluble sulfate concentration occurs, have broadly similar properties to the rest of the soils in the entire study area and are all covered by similar vegetation type. No other soil chemical property showed a clear trend with distance away from the power station.

The average base saturation in the 2000 soil samples was 78.6% compared to > 80% in the 1996 and 1999 soil samples. It must be emphasized here that in the calculations of base saturation only Ca and Mg were included as the major base cations. Sodium and K also contribute to base saturation in soils but were not taken into account. The slight difference might be as a result of the different sampling strategy adopted in 2000 or the non inclusion of all base cations in the calculations. Some studies of atmospheric deposition of pollutant gases have emphasized the role of base cations particulate matter especially fly ash and other alkaline material in neutralizing soil acidity and acidity of precipitation. This aspect was not considered in the current study. It will be important to make an inventory of the sources of alkaline dust in the region and determine its potential effect on the deposition of acidity.

Sampling beyond the 20 km radius from Arnot power station and in the opposing wind direction will be important in determining background soil properties against changes resulting from increased atmospheric deposition from the power station. Studies of soil organic carbon in uncultivated natural grassland soils in other parts of South Africa remote from atmospheric sulfur deposition will be important to see what differences exist between the two areas and perhaps establish the likely factors controlling accumulation.

REFERENCES

Alloway B J. 1995. *Heavy metals in soils.* (second edition). Blackie Academic. London. 368pp.

Always F J, Marsh A W and Methley W J. 1937. *Sufficiency of atmospheric sulfur for maximum crop yields.* Proc Soil Sci. Am. 2, 229-238.

Baker K F. 1976. *The determination of organic carbon in soils using a probe- colorimeter.* Laboratory Practice 25: 82-83.

Baldock J A and Nelson P N. 2000. *Organic matter.* In Malcolm E S (ed in chief). Handbook of soil science. CRC press.

Blaser P, Zysset M, Zimmermann S and Luster J. 1999. *Soil Acidification in Southern Switzerland between 1987 and 1997: A Case Study Based on the Critical Load Concept.* Environ. Sci. Technol. Vol. 33, no.14. 2383-2389

Bremner J M and Mulvaney C S. 1982. *Nitrogen-Total*[1]. In Page A L, Miller R H and Keeney D R. (eds.) Methods of soil analysis: Part 2-chemical and microbiological properties, 2nd edition. Am. Soc. Of Agron., Inc., Madison, Wisconsin USA.

Buckman H O and N C Brady. 1969. *The nature and properties of soil.* Seventh edition. The Macmillan company/Collier Macmillan Limited London.

Buhmann C. 1986. *Investigation of 2:1 layer silicate clays in selected Southern African soils.* PhD Thesis. Department of Soil Science and Agrometeorology, University of Natal, Pietermaritzburg.

Carter R M. 1993 (eds). *Soil Sampling and methods of analysis.* Lewis publishers.

Chishala B H, Mbewe D N, Msoni R and Kabwe H C. 1997. *A specialist environmental assessment of soil pollution in the vicinity of the Mufulira smelter and a soil survey at the konkola deep mining licence area in Zambia.* (Unpublished Research report).

Courchesne F, Laberg J F and Dufrense A. 1998. *Influence of soil organic matter on sulfate retention in two podzols in Quebec in Canada.* Canadian J. of soil Sc. 103-109.

Cresser M, Billet M, Skiba U. 1989. Cited in Blaser P, Zysset M, Zimmermann S and Luster J, 1999. *Soil Acidification in Southern Switzerland between 1987 and 1997: A Case Study Based on the Critical Load Concept.* Environ. Sci. Technol. Vol. 33, no.14. 2383-2389

Drever J I. 1997. *The geochemistry of natural waters: surface and groundwater environments.* 3rd ed. Prentice Hall Inc.

Du Toit B. 1993. *Soil acidification under forest plantations and the determination of the ANC of soils.* MSc Thesis. Faculty of Agriculture, University of Natal, Pietermaritzburg.

Ensminger L E. 1954. *Some Factors affecting the adsorption of sulfate by Alabama soils.* Soil Sc. Soc. of Am. Proc. 18, 259-264.

Fey M V and Netch A A. 1994. *Soil chemical assessment and alleviation of industrial impacts on the South African environment.* Annual progress report to ESKOM.

Fey M V, Echeverria M E, Whyte S, Abanda P A and van Tienhoven A M. 1999a. *Sensitivity of the soil environment to the deposition of acidifying air pollutants in South Africa.* Eskom Research Report No RES/RR/99/00174.

Fey M V, Manson A D and Schütte R. 1990. *Acidification of the pedosphere.* South African Journal of Science. Vol. 86. Page 403-406.

Fey M V, Vusi G and Nowicki T. 1999b. *Aluminium is stabilised by humus and sulphate in strongly acidified soils by tea and pine plantations.* Conference poster. Soil Science society of South Africa 22nd congress held at the University of Pretoria conference centre

Fey M V. 2000. *Personal communication.* Professor of Soil Science University of Stellenbosch.

Fey M V. and Guy S A. 1993. *The capacity of soils in the Vaal dam catchment to retain sulphate from atmospheric pollution.* Report to the Water Research Commission (Report No 414/1/93) by the Department of Agronomy, University of Natal.

Freney J R and Williams C H. 1983. *The sulfur cycle in soils.* In: Ivanov M V and Freney J R. 1983. The Global Biogeochemical Sulfur Cycle. Scientific committee on problems of the environment. (SCOPE) 19.

Freney J R, Melville G E and Williams C H. 1970. *The determination of carbon bonded sulfur in soils.* Soil Sc., 109, 310-318.

Galloway J N. 1995. *Acid deposition: Perspective in time and space.* Water, Air and soil pollution 85:15-24.

Grobler L, Bloem A A and Classens S A. 1999. A *critical soil sulphur level for maize (Zea mays L) grown in a glasshouse.* S. Afr. J. Plant Soil. 16(4).

Gustafsson J P. 1995. *Modelling pH-dependent sulfate adsorption in the B-s horizons of podzolized soils.* Journal of Environmental Quality v 24 pp 882-8.

Held G, Gore B J, Surridge A D, Tosen G R, Turner R C and Walmsey R D (eds). 1996. *Air pollution and its impacts on the South African Highveld.* Environmental Scientific Association, Cleveland, 144p.

Heynike J C. 1981. *The economic effects of the mineral content present in the Vaal River Barrage on the community of the PWV-Complex* (a desk study). Water Research commission, Pretoria. In Held G Gore B J, Surridge A D, Tosen G R, Turner R C and Walmsey R D (eds). 1996. *Air pollution and its impacts on the South African Highveld.* Environmental Scientific Association, Cleveland, 144p.

Huete A R and McColl J G. 1984. *Soil cation leaching by acid rain with varying nitrate –to-sulfate ratios.* Journal of Environmental Quality. 13:366-371.

Karltun E and Gustaffsson J P. 1993. *Interference by organic complexation of Fe and Al on the SO_4^{2-} adsorption in spodic B horizons in Sweden.* J of soil Sc., 44, 625-632.

Karltun E. 1994. *The determination of adsorbed sulfate with isotopic dilution of sulfur (^{35}S) compared with Calcium dihydrogen phosphate extraction.* Commun. Soil. Sc. plant. Anal., 25(3&4), 2 07-214.

Kempster P L, Skorowszewski R W, Roos G N and Gore B J. 1996. In Held G, Gore B J, Surridge A D, Tosen G R, Turner C R and Walmsley R D. (eds). *Air pollution and its impacts on the South African Highveld.* Environmental Scientific Association, Cleveland, 144pp.

Kuylenstierna J A. 1996. *Reports prepared by international delegates. Report on the impacts of air pollution on the quality of soil and water: A southern African perspective*, Johannesburg, 22-23 August 1996. Eskom Project No. 7760T127R.

Larssen T and Carmichael G R. 1999. *Acid Rain and acidification in China: The importance of base cation deposition.* Environmental pollution 110 (2000) 89-102.

Lukina N V and Nikonov V V. 1998. *Content and composition of humus in the northern Taiga Al-Fe-humus podzolic soils subject to atmospheric pollution.* Eurasian Soil Sci. 31, 6: 671-678.

McBride M B. 1994. *Environmental chemistry of soils.* Oxford University Press, New York.

McFee W W. 1980. *Sensitivity of soil region to the long-term acid precipitation. In: Atmospheric sulfur deposition. Environmental impacts and health effects.* Ann Abor Science Publishers Inc., Ann Abor, MI.

Meyer J H, Wood R A and Du Preeze P. 1971. *A nutrient survey of sugarcane in the South African sugar industry.* Proc. S. Afric. Sug. Technol. Ass. 45, 196-204.

Moss M R. 1975. *Spatial patterns of sulfur accumulation by vegetation and soils around industrial centres.* J. of Biogeography. 2 205-222.

Nelson D W, and Sommers L E. 1982. *Total carbon, organic carbon and organic matter.* In: Methods of soil analysis. Part 2, 570-571. Am. Soc. Argon. Madison, Wisconsin.

Nodvin C S, Driscoll C T and Likens G E. 1986. *The effect of pH on sulfate adsorption by a forest soil.* Soil Science Vol. 142, No. 2, 69-75.

Nowicki T E. 1997. *The impact of plantations of pinus spp. on the chemical properties of soils and stream waters in South African upland catchments.* PhD thesis, University of Cape Town.

O'Brien R D. 2000. The Neutralisation of acid mine drainage by fly ash. Unpublished MSc. thesis, Environmental Geochemistry at the University of Cape Town.

Olanyinka, Adebayo A and Amusan A. 1998. *Evaluation of Organic carbon oxidation of a modified wet combustion and Walkley Black procedures in Nigerian soils.* Commun. in soil sci. plant anal. 29 (17 and 18), 2749-2756.

Pidwirny M J. 1996. *Fundamentals of physical geography.* Online textbook. http:/www.geog.ouc.bc.ca/phys geo/home html.

Pockock F. 2000. *Personal communication.* XRF analyst Department of Geological Science University of Cape Town.

Pretorius R W, Auret I, Held G, Brassel K M, Danford I R and D D Waldie. 1986. *The climatology of the boundary layer over the Eastern Transvaal highveld and its impact on sulphur dioxide concentrations at ground level.* CSIR Report Atmos/86/16, Pretoria, 212pp.

Reuss J D. 1975. *Chemical and biological relationship relevant to the effect of acid rainfall on the soil-plant system.* In proceedings of the first international symposium on acid Precipitation and forest ecosystem. USDAFS Tech. Report- Ne-23

Reuss J O and Johnson D W. 1986. *Acid deposition and the acidification of soils and waters.* Springer-Verlag, New York.

Reuss J O, Cosby B J and Wright R F. 1987. *Chemical processes governing soil and water acidification.* Nature 329: 27-29.

Rhoades J D. 1982. *Soluble salts*. In Page A L, Miller R H and Keeney D R (eds.). Methods of soil analysis: Part 2.167-171. Am.Soc. Agron. Madison, Wisconsin.

Schaaf W, Weisdorfer M and Huettl R F. 1995. *Soil solution chemistry and element budgets of three scots pine ecosystems along a deposition gradient in North Eastern Germany*. Water, Air and Soil Pollution 85:1197-1202.

Schloemann H. 1994. *The Geochemistry of some Western Cape soils (South Africa). With emphasis on toxic and essential elements*. PhD thesis. University of Cape Town.

Seip H M. 1980. *Acidification of fresh water: Sources and mechanisms* p 358-36. In: Drablos and A Tollan (ed.) Proceedings of international conference of ecological impacts of acid precipitation. SNSF- Project Oslo- Norway.

Singh B R. 1982. *Sulfate sorption by acid forest soils: 2. Sulfate adsorption isotherms with and without organic matter and oxides of aluminium and iron*. Soil Science. Vol. 138, No. 4.

Skoroszewski R W. 1995. *Sulphate deposition to a small upland catchment at Suikerbosrand, South Africa.* Water, Air and Soil Pollution 85:2331-2336.

Soil classification working group. 1991. *Soil Classification. A Taxonomic system for South Africa*. Soil and agricultural department, Pretoria.

Sposito G and Reginato R J. 1992. *Opportunities in Basic Soil Science Research*. Soil Science Society of America, Inc. Madison, Wisconsin, USA.

Sposito G. 1989. *The chemistry of soils*. Oxford University Press, New York, Inc.

Starkey R L. 1966. Oxidation and reduction of sulfur compounds in soils. Soil Sc. 101, 297-306.

Stotzky G and Norman A G. 1961. *Factors limiting microbial activity in soils*. Ll. The effect of sulfur. Cited in Freney J R, Melville G E and Williams C H. 1970. *The determination of carbon bonded sulfur in soils*. Soil Sc., 109, 310-318.

Sumner M E, Fey M V and Noble A D. 1991. *Nutrient Status and Toxicity Problems in acid soils*. In: Ulrich B and Sumner M E (eds). Soil Acidity. Springer Verlag Berlin, Heidelberg.

Tabatabai M A. 1982. Chapter 28 - *Sulphur*. In: Methods of Soil Analysis - Part 2 - Chemical and Microbiological Properties. Agronomy Monograph 9. Second edition. ASA-SSSA, Madison, WI. pp1159.

Tabatabai M A. 1987. *Physiochemical fate of sulfate in soils*. JAPCA 37:34-38

Theron J J. 1961. *Die herstel van humus deur middel van bemeste grasrusoeste. S. Afric. J. Agric Sci*. 4, 415-430.

Thomas G W. 1982. Chapter 9 – *Exchangeable cations*. In methods of soils analysis – Part 2 - Chemical and Microbiological Properties. Agronomy Monograph 9. Second edition. ASA-SSSA, Madison, WI. pp.1159.

Turner C R, Wells R B and Olbrich K A. 1996. *Deposition chemistry in South Africa*. In: Held G, Gore B J, Surridge A D, Tosen G R, Turner R C and Walmsey R D (eds). Air pollution and its impacts on the South African Highveld. Environmental Scientific Association, Cleveland, 144p.

Tyson P D, Kruger J F and Louw C W. 1988. *Atmospheric pollution and its implications in the Eastern Transvaal Highveld.* South African National Scientific Programmes. Report No 150. CSIR Pretoria.

Ulrich B and Sumner M E. 1991 (eds). *Soil Acidity.* Springer Verlag Berlin, Heidelberg.

van Tienhoven A M. 1997. *Assessment of long-term air pollution impacts on soil properties in the vicinity of Arnot power station on the South African Highveld.* Unpublished MSc. thesis, Environmental Geochemistry at the University of Cape Town.

Walkley A and Black I A. 1934. *An examination of the Degtjareff method for determining soil organic matter and a proposed modification of the chromic acid titration method.* Soil Sci. 37:29-38.

Walkley A. 1935. *An examination of methods for determining organic carbon and nitrogen in soils. J. Agr. Sci.* 25, 598-609.

Wells R B, Llyod S M and Turner. 1996. *National Air pollution Source inventory* (*Inventory of scheduled processes*) In: Held G, Gore B J, Surridge A D, Tosen G R, Turner R C and Walmsey R D (eds) 1996. *Air pollution and its impacts on the South African Highveld.* Environmental Scientific Association, Cleveland, 144p.

Williams C H. 1974. *The chemical nature of sulphur in some New South Whales soils.* Cited in Freney J R and Williams C H. 1983. *The sulfur cycle in soils.* In: Ivanov M V and Freney J R. 1983. The Global Biogeochemical Sulfur Cycle. Scientific committee on problems of the environment. (SCOPE) 19.

Zunckel M, Turner C.R and Wells R B. 1996. *Dry Deposition of sulfur over the Mpumalanga Highveld: a pilot study using the inferential method.* South African J of Sc. Vol. 92 485-491.

Zunckel M. 1998. *Dry deposition of Sulfur over eastern South Africa.* Atmospheric Environment 33: 3515-3529.

APPENDIX A

ANALYTICAL METHODS

A1.1 Preparation of saturated paste extracts

Saturated pastes extracts were prepared using 200 g of air-dried soil. Sufficient distilled water was added to the soils to reach saturation. The soils were allowed to equilibrate overnight before extraction. The extractions were done on a vacuum line using Whatman number 50 filter paper on a Buchner funnel. The pH and EC of the saturated pastes extracts were obtained and the extracts filtered through a 0.45 μm Millipore filter and diluted and used for various analyses. Excess sample was stored in a refrigerator for repeat analysis where necessary.

A1.2 Determination of soil pH

1.2.1 pH in water and in 1 M KCl solution

The pH of the samples was measured using two different techniques. Firstly, pH measurements were performed on a 1:2.5 soil to solution ratio. 10g of air-dried sample and 25 ml of 1 M KCl solution distilled water was put on a reciprocating shaker and allowed to equilibrate for ten minutes. The pH of the supernatant was measured using a Metrohm 691 pH meter. The procedure was repeated using distilled water. At least two measurements were performed for each sample and the average taken.

1.2.2 pH of saturated paste extracts

Secondly the pH of saturated paste extracts was measured after extraction. The pH was measured using a Metrohm 691 pH meter. The meter was calibrated using standard metrohm buffers of pH 7.0 and pH 4.0, (± 0.02 pH units at 25°C). At least two measurements were performed for each sample and the average taken.

A1.3 KCl extractable acidity determination

KCl extractable acidity was determined according to the method by Thomas (1982). 25 ml of 1 M KCl was added to 2.5 g of air-dried soil in 100 ml centrifuge tubes and put on a reciprocating shaker for about 30 minutes. The mixture was centrifuged at 2000 rpm for 5 minutes and filtered through a 0.45 μm cellulose acetate millipore filter membrane. A blank of 25 ml 1 M KCl solution was titrated with standard 0.01 M NaOH solution and used as a correction factor. The standard 0.01 M NaOH solution was then used to titrate the supernatant of a 2.5g air-dried soil sample and 25 ml 1 M KCl mixture. Phenolphthalein was

used as an indicator while checking the endpoint pH, which was around 8.3. The volume of NaOH needed to neutralise the acidity (corrected for by the result obtained using the blank) was recorded and the number of moles of NaOH was calculated. The following formula was used to calculate acidity in $mmoles_c$/kg of soil:

$concentration_{NaOH} \times (volume_{NaOH} - volume_{blank}) = mmoles_{NaOH} = mmoles_{acidity}$

$mmoles_{acidity} / volume_{supernatant} = molar\ concentration_{acidity}$

$concentration_{acidity} \times (volume_{KCl}/mass_{sample}) = exchangeable\ acidity\ (mmoles_c/kg\ soil)$

The remaining supernatant was diluted 10 times and submitted for exchangeable base cations (Mg and Ca) determination by atomic absorbsion spectroscopy (AAS see below).

A1.4 Calcium and Mg determination by atomic absorption spectroscopy (AAS)

10 ml of the filtered supernatant solution prepared for acidity titration was diluted 10 times. Atomic Absorption Spectroscopy (AAS) was used to determine Ca and Mg concentrations with standards prepared in 0.01M KCl solution. The liquid samples were nebulised, before being aspirated into a flame, (Temperature 2 000 – 3 000 K), and then they were atomised. Ground state atoms absorb energy in the form of light of a specific wavelength and are elevated to an excited state. The amount of light energy absorbed at this wavelength will increase as the number of atoms of the selected element in the light path increases. The concentration of an element in the original sample can be determined by relating the amount of light absorbed to that of the element in a standard of known concentration. Duplicate samples were analysed to check reproducibility of the method.

A1.5 Electrical conductivity (EC)

The EC of recovered filtrate from the saturated paste was measured using an RE 387 TX microprocessor conductivity meter consisting of a conductivity cell and temperature probe. The meter was calibrated using a 0.1N KCl solution with a conductivity of 141.2 mS/m and the measured conductivity was reported in µS/cm. At least two measurements were performed for each sample and the average was taken as EC of the saturated paste extracts.

A1.6 Total organic carbon: Hot digestion/colorimetric method involving heating of sample

Total organic carbon was measured according to the method of Baker (1976). This method is suitable for all soils except in soils with organic carbon less than 0.2%. 1.0 g of air-dried swing-milled soil sample (< 0.15 mm) was transferred into 100 ml digestion tubes. The sample was mixed with 2 ml of distilled water and 10 ml $K_2Cr_2O_7$ solution and stirred to allow H_2O and dichromate mixture to completely wet the soil. 5 ml of concentrated H_2SO_4 was slowly added to the solution and digested on a digestion block at 150 °C for 30 minutes. After digestion, the sample was allowed to cool, 50 ml of 0.4% barium chloride was then added, the mixture was swirled to ensure thorough mixing and then allowed to stand overnight. Six standards were prepared in the same fashion having a range of carbon (0, 5, 10, 15, 20, and 25 mg C). An aliquot of the supernatant liquid after standing overnight was transferred into a colorimeter cuvette. The absorbance of standards, blanks and samples were measured at 600 nm. Measurements were done on a Spectronic 20 Genesys spectrophotometer. Absorbance against standard concentration was plotted (Figure A1) from which the solution concentrations were determined for each unknown after subtraction of the mean blank value from the unknowns to give a corrected concentration value (K).

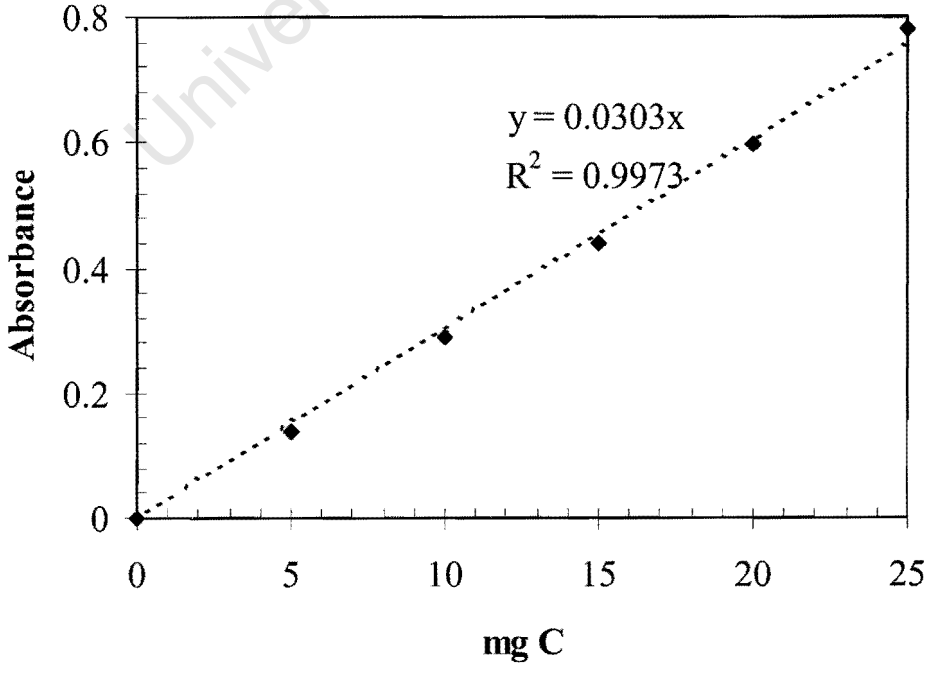


Figure A 1. Calibration curve for organic carbon determination

Calculations

The percentage organic carbon was calculated as

% Organic carbon = (K x 0.1) / W, where W = weight of soil.

A1.7 Total carbon analysis

Total carbon analysis was done by the Dumas or dry combustion method for the determination of total carbon, total nitrogen and total sulphur in soils (Bremner and Mulvaney, 1982)

Exactly 0.5 g of sample air-dried and sieved (< 2 mm) was weighed into a ceramic boat. 1.0 g of Com-cat (mixture of metal oxides) was added and stirred. The boat was introduced into a horizontal furnace and the sample roasted in a stream of oxygen at 1350 °C. The resultant combustion gas was collected and after removal of moisture, carbon was measured as carbon dioxide by means of infrared. After each sample, the carbon dioxide produced from the combustion process and the oxygen used for roasting the sample are stripped using a stream of nitrogen gas.

A1.8 Major cations and anions: ion chromatography (IC)

Ion chromatography is an analytical technique for the separation and determination of ions in solution. An eluent is passed through a solid stationary phase consisting of ion exchange resin beads packed into a cylindrical column. A high-pressure pump is required to force the eluent through the column. In-line detection of the separated ions of interest is achieved by monitoring conductivity.

Analyses for anions and cations within saturated paste extracts were carried out using a Dionex DX300 series suppressed IC system coupled to an AI-450 chromatography software package. The run conditions were as follows:

Sample loop volume: 50 µl
Gurad column: Dionex HPIC-IonPac AG4A
Separator column: Dionex HPIC-IonPac AS4A-SC
Eluent: 1.80mM Na_2CO_3 and 1.70 mM $NaHCO_3$
Eluent flow rate: 2.0 mL.minute^{-1}
IC was used to determine the following major cations (Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+} and NH_4^+) and anions (SO_4^{2-} Cl^-, and NO_3^-) concentrations in the saturated paste extracts. The extracts

were passed through 0.45 μm cellulose acetate millipore filter membranes. Samples were diluted such that their electrical conductivities were below 100 μS/cm.

A1.9 Mineralogical analysis of clay fraction - X-ray diffraction spectroscopy

The clay fractions of the samples were separated in order to prepare samples for mineralogical analysis by XRD. Approximately 20 g of sample was placed in 500 ml glass beakers and about 300 ml distilled water was added in order to make a liquid slurry. The mixture was ultrasonicated with an ultrasound probe for about 5 minutes. A 63-micron sieve was used to separate the sand fraction of the mixture from the mud fraction. The separated sand fraction was dried in the oven at 60 °C. The slurry was resuspended in a 3% sodium hexametaphosphate solution to separate the clay fraction from the silt fraction. The supernatant liquid containing the suspended clay was transferred into centrifuge bottles and centrifuged at 5000 rpm for ten minutes. The somewhat clear supernatant was discarded and the concentrated clay smeared evenly across a glass slide and allowed to dry prior to analysis.

The glass slides were scanned over a 2θ angle range of 4 – 75°, using a step size of 0.5° and step duration of one second. The samples were irradiated by means of monochromatic X-rays emitted by a copper tube [λ (K_α) = 1.54056 Å]. The generator was run at 25 mA current and a potential of 40 kV.

A1.10 Determination of soil moisture content and loss on ignition (LOI).

About 5 g of air dried soil was placed into preweighed and preheated porcelain crucibles and put in the oven at 110 °C for 4 hours. The samples were then removed and allowed to cool for about 30 minutes in a dessicator after which they were weighed. The weight after heating was recorded as Y and the moisture content was calculated the difference in weight after heating over the initial weight multiplied by 100.

$$\text{Moisture content (\%)} = \frac{\text{(weight of air dried sample - weight of oven dried soil)}}{\text{weight of air-dried sample}} \times 100$$

Percentage moisture content was based on only one determination per sample. About 5 g of air dried soil was placed into preweighed and preheated porcelain crucibles and roasted overnight at about 900 °C. The samples were quickly taken out of the furnace and allowed to cool in a dessicator after which the weight loss was measured and recorded. The LOI was calculated as:

(Weight loss after roasting/ weight of air dried soil) x 100

This was recorded as a percentage. The moisture content and LOI were used as a correction factor for generating mass absorption coefficients used in calculating the percentages of major elements in the powder briquettes and trace sulfur concentration. Major elements are measured using fusion discs, which minimizes errors resulting from sample preparation and from the presence of organic matter and water in the sample. Measurements of major elements on powder briquettes necessitated the measurements of LOI and moisture content to account for organic mater and water in the sample. Despite the use of powdered briquettes in generating majors the total were around 95-98 %, according to (F. Pockock pers. comm. 2000) is very good and therefore reliable. Matrix effects that result from the irregularity of the sample surface could account for the difference.

A1.11 Preparation of powder briquettes for major and trace element (S) analyses

Powder briquettes for X-ray fluorescence spectroscopy were prepared according to the standard method employed by the Department of Geological Science at the University of Cape Town, as follows

About 60 g of air-dried soil was sieb swing milled using a carbon steel vessel for two minute at a fast setting. Plastic gloves and wooden spatula was used to transfer the milled samples into labelled plastic bags and sealed. To ensure that samples were not contaminated, the sieb mill was cleaned between samples by milling with quartz for one minute. The milled quartz was discarded and the mill cleaned with compressed air. The vessel was then washed under tap water, and rinsed with distilled water and finally dried with acetone. The milled samples were used to prepare briquettes, which were put under a vacuum for about thirty minutes to test their strength to ensure that they don't shatter in the XRF instrument. Briquettes were prepared by subjecting the samples under a pressure of about ten tonnes. A boric acid backing was used to hold the sample firm since these soils were mostly sandy soil with little clay. To reduce matrix effects, which result from uneven briquette surfaces, the samples were milled as fine as possible. Matrix effect problems are limited to elements with atomic number less than Z=19 (i.e. potassium) with this method. This method is therefore regarded as semi-quantitative, with accuracy to within 3%.

During analysis the briquettes are irradiated by a beam of short-length X-rays with a Philips wavelength dispersive XRFS. A photon of the incident ray ionises inner orbital electrons and upon relaxation, fluorescent X-rays are emitted. Each element has characteristic 2θ values at which they will emit X-rays according to the Bragg equation: $n\lambda = 2d\sin\theta$

Table A.1 Analytical conditions for determination of major elements using Phillips PW 1480 WDXRF spectrometer.

Element line	*Collimator*	*Crystal*	*Detector*	*PHS*		*Counting Time (s)*	*Concentration range*	*RMS*	*No. of standards*
				LWL	UPL				
FeK∝	F	LiF(220)	FL	16	70	150	0 – 17	0.118	14
MnK∝	F	LiF(220)	FL	15	70	150	0 – 0.22	0.005	14
TiK∝	F	LiF(220)	FL	28	70	150	0 – 2.75	0.020	14
CaK∝	F	LiF(220)	FL	36	70	20	0 – 12.5	0.037	14
K K∝	F	LiF(220)	FL	36	70	50	0 - 15.5	0.057	14
P K∝	C	GE(111)	FL	25	75	100	0 – 0.36	0.008	14
SiK∝	C	PE(002)	FL	32	74	100	0 – 100	0.408	14
Al K∝	C	PE(002)	FL	25	75	80	0 – 17.5	0.136	14
MgK∝	F	PX-1	FL	30	74	150	0 - 46	0.095	14
NaK∝	F	PX-1	FL	30	78	200	0 - 9	0.189	15

Table A.2 Soil moisture content (H_2O) and loss on ignition (LOI)

Sample	LOI (%)	H_2O (%)
A 1 (0-10)	5.63	1.81
A 1 (10-20)	8.09	1.45
A 1(20-30)	7.61	1.53
A 1 (30-40)	8.00	1.71
A 2 (0-10)	5.20	1.22
A 2 (30-40)	3.92	1.02
A 3 (0-10)	2.48	0.37
A 3 (30-40)	2.08	0.44
A 4 (0-10)	11.64	**18.23**
A 5 (0-10)	6.05	0.76
A 5 (20-30)	6.11	0.80
A 6 (0-10)	5.66	0.85
A 6 (10-20)	7.84	2.21
A 10 (0-10)	9.49	3.04
A 10 (30-40)	11.83	5.59
A 12 (0-10)	6.92	1.24
A 12 (10-20)	5.43	1.95
A 12 (20-30)	5.11	1.30
A 15 (0-10)	4.96	0.98
A 15 (30-40)	5.95	0.65
A 16 (0-10)	5.66	0.88
A 16 (20-30)	4.10	0.57
A 17 (0-10)	17.29	10.27
A 17 (30-40)	2.66	0.45
A 18 (0-10)	7.18	1.10

Table A.2 Soil moisture content (H_2O) and loss on ignition (LOI)

Sample	LOI (%)	H_2O (%)
A 18 (10-12)	5.17	0.82
A 18 (20-30)	4.25	0.63
A 18 (30-40)	4.24	0.68
A 18 (40-50)	4.35	0.66
A 19 (0-10)	2.48	0.29
A 19 (30-40)	2.19	0.29

Table A.3 Total sulfur data from Van Tienhoven (1997) and Fey *et al.* (1999a)

Sample profile	Distance.from power station (km)	1999 (%)	1996 (%)
Topsoil			
A1	19.9	0.05	0.04
A2	16.9	0.03	0.02
A3	14.8	0.02	0.02
A4	12.8	0.06	0.05
A5	10.7	0.06	0.04
A6	1.3	0.03	0.03
A7	8.1	0.03	0.02
A8	14.4	0.04	0.03
A9	12.6	0.04	0.04
A10	8.3	0.05	0.04
A11	4.5	0.03	0.03
A12	5.5	0.05	0.04
A13	5.8	0.02	0.01
A14	18.8	0.02	0.02
A15	1	0.03	0.03
Subsoil			
A1	19.9	0.03	0.03
A2	16.9	0.02	0.02
A3	14.8	0.01	0.01
A4	12.8	0.04	0.03
A5	10.7	0.04	0.03
A6	1.3	0.03	0.03
A7	8.1	0.02	0.01
A8	14.4	0.03	0.02
A9	12.6	0.03	0.02
A10	8.3	0.04	0.02
A11	4.5	0.02	0.01
A12	5.5	0.02	0.02
A13	5.8	0.01	0.01
A14	18.8	0.02	0.02
A15	1	0.02	0.02

APPENDIX B

DESCRIPTION OF THE SAMPLING SITES

The sites sampled for this study were surveyed and marked on a 1:50 000 topographical sheet of the Arnot area (Department of Land affairs surveys and mapping). These sites had been marked with painted bricks and could easily be located. An attempt has been made to group the soils into soil forms based on the South African system of soil classification from observations made in the field. Detailed description of the earlier 15 sites selected and sampled be found in van Tienhoven, (1997). Only soils that were analysed for this study have been considered. Topographic sheets were obtained from the Department of Land affairs, Surveys and mapping in Cape Town. The soil samples are stored in the University of Stellenbosch.

Site A1

Date of sampling	17/07/2000
Position Longitude	29° 59' 18.2'' E
Latitude	25° 55' 05.1'' S
Topographic sheet	2599 DD Arnot
Radius from power station	19.9 km east-north east of the power station
Samples collected by	Azah, Grace and Elias
Soil form	Bainsvlei form
Soil family	1100 morning side family
Parent material	Quartzite and shale or diabase
Vegetation	Short grassland that has been grazed recently by cattle
Soil colour matrix	Reddish iron oxide coloration
Horizonation	An orthic A horizon overlies a red brown apedal B horizon and the transition from the orthic A to red apedal B-horizon is very diffuse making the recognition of distinct horizons difficult. Below the red apedal B-horizon is a soft plinthic B horizon at about 60 cm from the surface.

Observations

Area looks overgrazed by cattle. Cattle were present on site during the day of sampling. Soil profile showed no signs of mechanical disturbance or the presence of water table. Large outcrops of rocks found on site and also some lateritic crusts.

Site A2

Date of sampling	17/07/2000
Position Longitude	29° 57' 22.4''E
Latitude	25° 56' 16.5''
Topographic sheet	2599 DD Arnot
Radius from power station	16.9 km east of power station
Samples collected by	Azah, Grace and Elias
Soil form	Avalon form
Soil family	Blackmoor
Parent material	Shale
Vegetation	Tall grass field height between 50-70 cm with no signs of recent grazing.
Soil colour matrix	An orthic A horizon overlies a yellow brown apedal B horizon
Horizonation	An orthic A horizon overlies a yellowish brown apedal B horizon

Observations

The soil was moist with a fine and loose texture and showed no signs of disturbance or water table. Soil profile looks very deep since the soft plinthic layers common to most profiles in this area was not reached at the depth of sampling (50 cm). Wattle trees border South side of sampling point.

Site A3

Date of sampling	17/07/2000
Position Longitude	29° 55' 55.2'' E
Latitude	25° 54' 46.9'' S
Topographic sheet	2599 DD Arnot
Radius from power station	14.8 km north east of power station
Samples collected by	Azah, Grace and Elias
Soil form	Avalon form
Parent material	Basalt and andesite
Vegetation	Natural undisturbed grassland
Horizonation	An orthic A-horizon overlies a yellow brown apedal B horizon that grades into a soft plinthic horizon below. The transition from the A to the B-horizon was diffuse.

Observations

Soil profile showed no signs of wetness. Plant roots are prominent in the first 10 cm of the soil profile.

Site A4

Date of sampling	17/07/2000
Position Longitude	29° 54' 34.1 E
Latitude	25° 54' 15.3''S
Topographic sheet	2599 DD Arnot
Radius from power station	12.8 km north east of power station
Samples collected by	Azah, Grace and Elias
Soil form	Dressen form
Soil family	Tevreden
Parent material	Basalt and andesite
Vegetation	Natural grassland
Horizonation	Orthic A horizon overlies a hard plinthic B horizon and beyond 40cm depth the soil was too hard to obtain

Observations

This sample site is located on the north facing side of Grootpan, which is the direction from which the dominant winds blow. The soil profile was quite shallow when compared to other profiles, which are located downwind of the pans. It is assumed that material gets eroded from the pans and is deposited on the edges during dry periods of the year when the pans are dry or when the water level falls.

Site A6

Date of sampling	19/07/2000
Position Longitude	29° 47' 53.3'' E
Position Latitude	25° 56' 0.8.5''S
Topographic sheet	2599 DD Arnot
Radius from power station	1.3 km, north east of the power station.
Samples collected by	Azah, Grace and Elias
Soil form	Dresden form
Parent material	Shale
Vegetation	Absence of any real vegetation
Soil colour matrix	Reddish soil
Horizonation	Orthic A horizon overlying a plinthic B-horizon. Transition to the B horizon is diffuse

Observations

A huge coal stockpile was present a few hundred meters on the western side of the site. The vegetation on this was burned a few days prior to sampling. Soil looked dry and showed no signs of mechanical disturbance. Only two samples were obtained from this site due to the shallow depth of the profile. Beyond 20 cm in the profile, a hard plinthic layer was reached.

Site A7

Date of sampling	19/07/2000
Position Longitude	29° 51' 34.5'' E
Latitude	25° 54' 30.6'' S
Topographic sheet	2599 DD Arnot
Radius from power station	8.1 Km, south east of the power station.
Samples collected by	Azah, Elias, Grace,
Soil form	Pinedene form
Soil family	Goudini
Parent material	Shale
Vegetation	Natural grassland vegetation
Soil colour matrix	Dark colour

Observations

This soil had a fine sandy texture and exhibited some degree of wetness. The water table was not reached even though soil showed signs of wetness. The transition from the A to the B horizon was very smooth. The topsoil had a characteristic dark colour that was different from the majority of soils from this area.

Site A10

Date of sampling	17/07/2000
Position Longitude	29° 51' 55.3'' E
Latitude	25° 58' 29.8'' S
Topographic sheet	2599 DD Arnot
Radius from power station	8.3 km east south east of the power station
Samples collected by	Elias, Azah, Grace,
Soil form	Milkwood form
Soil family	Effingham
Parent material	Dolerite
Vegetation	Natural undisturbed grassland.
Soil colour matrix	Dark or melanic colour 10YR 3/3
Horizonation	Melanic A horizon overlying a lithocutanic B-horizon. The transition from the A to the B horizon is very sharp. The A horizon extends down to about 40 cm in the profile. The soil was moist and clayey.

Observations

This soil profile looks different from the rest of the profiles sampled for this study. The soil is a dark soil and very sticky. The vegetation was quite dense and the area looked undisturbed. Soil looks undisturbed but the presence of worm burrows is worth mentioning since this aid in mixing of the soil to some extent.

Site A12

Date of sampling	17/07/2000
Position Longitude	29° 50' 28.0'' E
Latitude	25° 55' 55.2'' S
Topographic sheet	2599 DD Arnot
Radius from power station	5.5 Km, east-north east of the power station.
Samples collected by	Azah, Grace, and Elias.
Soil form	Glencoe form
Soil family	Leeupan family.
Parent material	Shale
Vegetation	Natural vegetation that has recently been grazed by cattle
Soil colour matrix	Yellow Brown.

Observation

Soil profile only extended down to about 40 cm depth. No signs of water table or mechanical disturbance of the profile was observed.

Site A13

Date of sampling	16/07/2000
Position Longitude	29° 49' 56.9'' E
Latitude	25° 58' 44.4'' S
Topographic sheet	2599 DD Arnot
Radius from power station	5.8 km, south-west of the power station.
Samples collected by	Fey, Azah, Grace and Elias.
Soil form	Glencoe form.
Soil family	Leeupan family.
Parent material	Shale.
Soil colour matrix	Yellow Brown.

Observations

The soil profile was deep. Five samples were obtained up to a depth of 50 cm. The soil profile looked undisturbed and showed no signs of a water table.

Site A15

Date of sampling	16/07/2000
Position Longitude	29° 47' 05.2'' E
Latitude	25° 57' 20.7'' S
Topographic sheet	2599 DD Arnot
Radius from power station	1.0 km, south-south west of the power station.
Samples collected by	Azah, Grace, Elias
Soil form	Avalon form
Parent material	Shale.
Vegetation	Natural grassland.
Soil colour matrix	Yellow Brown

Observations

Deep soil profile reached up to one meter depth without coming in contact with a plinthic layer. Soil showed no signs of disturbance and water table.

Site A16

Date of sampling	16/07/2000
Position Longitude	nd
Latitude	nd
Topographic sheet	2599 DD Arnot
Radius from power station	3 km east-north east of power station
Samples collected by	Azah, Grace and Elias
Soil form	Glencoe form
Parent material	Shale
Vegetation	Natural grassland vegetation. Field not exposed to cattle.
Soil colour matrix	

Observations

This site is located about 500m from Rietkuil gate. The field from which sample was collected is fenced. Soil profile only extends to about 40 cm. Below this depth contact was made with fresh rock. Rock outcrops are common near the sampling site. The site is wedged near a telephone line.

Site A17

Date of sampling	17/07/2000
Position Longitude	nd
Latitude	nd
Topographic sheet	2599 DD Arnot
Radius from power station	4 km east-north east of the power station
Samples collected by	Azah, Grace and Elias
Soil form	Avalon form
Parent material	Shale
Vegetation	Thick natural grassland

Site A18

Date of sampling	17/07/2000
Position Longitude	nd
Latitude	nd
Topographic sheet	2599 DD Arnot
Radius from power station	6 km north of the power station.
Samples collected by	Azah, Grace and Elias

Site observations and description of soil profile

Soil form	Avalon form
Parent material	Shale
Vegetation	Thick grass field but showed signs of recent grazing

Observations

The soil was moist and had a blocky structure in the top horizon. The blocky structure graded to a fine sand texture in the subsoil. The soil showed no signs of mechanical disturbance or the presence of a water table. North of the site is a millies farm and south of the south is cattle feeding spot. The site is located below a power line and about 5o cm from the main road.

Site A19

Date of sampling	17/7/200
Position Longitude	nd
Latitude	nd
Topographic sheet	2599 DD Arnot
Radius from power station	6 km south of the power station
Samples collected by	Azah, Grace and Elias
Soil form	Avalon form
Parent material	Shale
Vegetation	Grass filed cleared for cattle feed

Observations

This site was located in an open field wedged between a power line to the east and a telephone line to the west. Access is through a back-wired fence about 20 metres from the main road (Hendrina road). The field looks overgrazed by cattle. The soil was moist, loose and made up mainly of fine sand material. Soil profile appears very deep.